Integrated Treatment Processes

For

Primary Wool Scouring Effluent

A thesis

submitted in fulfilment

of the requirements for the Degree of

Doctor of Philosophy in

Chemical and Process Engineering

by

Matthew J. Savage B.E.Hons.

University of Canterbury

December 2002

ABSTRACT

The increasing cost of effluent treatment in the wool scouring industry is rapidly becoming a determining factor in the viability of existing scouring operations and new installations alike.

This thesis details the development of an integrated effluent treatment process capable of treating the worst polluted effluent from a wool scour "heavy flow-down", to the point where it can either be economically discharged to local trade waste sewer, or directly discharged to river or ocean outfall with minimal environmental impact.

The existing proprietary chemical flocculation process, Sirolan CF™, was improved by the addition of a bio-flocculation stage and turbidity monitoring and control, and the product from this process fed to an aerobic biological treatment system based upon the traditional activated sludge process.

The biological treatment process was found to remove up to 98% of the BOD_5 loading from the pre-treated liquor with a hydraulic residence time of at least 50 hours being required in the aerobic digestion vessels. A residual biorefractory COD of approximately 3,600mg/L was identified which could not be removed by biological treatment. When operating continuously, the biological process was observed to metabolically neutralise the pH 3.0 – 4.5 feed from the chemical flocculation system to pH > 7.0 without the need for supplemental addition of neutralising agents such as sodium hydroxide. This in itself provides a significant economic incentive for implementation of the process.

Kinetic analysis of the biological process carried out under controlled laboratory conditions using a Bioflo 3000 continuous fermentor showed that the bio-chemical process followed substrate inhibition kinetics. An appropriate kinetic model was identified to represent the behaviour of the substrate degradation system, and modified by inclusion of a pseudo toxic concentration to account for the effect of pH inhibition upon the biological growth rate.

The process was verified both at pilot plant scale and at demonstration plant scale at an operational wool scour. The demonstration plant was of sufficient size to handle the full heavy effluent flow-down from a small wool scour.

At the time of publishing three full-scale effluent treatment systems based on this research had been sold to both domestic and international clients of ADM Group Ltd. who funded the research.

" . . . more hearts and bank balances have been broken on effluent treatment and wool grease recovery than on any other problem connected with the wool industry."

- Industrial Chemist (Truter 1956)

ACKNOWLEDGEMENTS

Without the support, assistance, and motivation provided by those around me, this undertaking would have never come to fruition. In particular I wish to thank:

My supervisor Professor Laurence Weatherley, who helped keep me on track over the last four years and guided the content of this thesis into a publishable form.

Technology New Zealand, and **ADM Group Ltd. Timaru**, who contributed extensive funding to the project. In particular, Tony Hadfield and Lindsay Halliday who were instrumental having the funding approved.

All of the staff at ANDAR, whose technical expertise and time were given enthusiastically to the furthering of this research and the commercialisation of its outcome.

The technical Staff of the University of Canterbury, department of Chemical and Process Engineering, whose technical and laboratory assistance ensured smooth progress throughout.

Jocelyn, Neil, Colin and Wendy, who supported, assisted, and housed me throughout much of the thesis process.

All my friends and particularly flatmates, who kept me encouraged and sane throughout the four years of research and thesis writing.

And thanks especially to my wife Sarah, whose support and understanding have been exceptional throughout this undertaking, particularly when the research called for extended periods of work abroad on extremely short notice.

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COMMON ABBREVIATIONS USED

BOD_5	Biological Oxygen Demand, 5-day test [mg/L]
COD	Chemical Oxygen Demand [mg/L]
SS	Suspended Solids [mg/L]
TS	Total Solids [mg/L] or [%]
SE	Solvent Extractables [mg/L]
TKN	Total Kjeldahl Nitrogen [mg/L]
MLSS	Mixed Liquor Suspended Solids [mg/L]
DRP	Dissolved Reactive Phosphorus [mg/L]
VM	Vegetable Matter
RO	Reverse Osmosis
CF	Chemical Flocculation
CF-B	Biological Treatment of Chemical Flocculation Effluent
DAF	Dissolved Air Flotation
WGR	Wool Grease Recovery
MVR	Mechanical Vapour Recompression
SWIMS	Scour Waste Integrated Management System
CSTR	Continuous Stirred Tank Reactor
HRT	Hydraulic Residence Time
SRT	Solids Residence Time
PID	Proportional – Integral – Differential Process Controller
PLC	Process Logic Controller
WRONZ	Wool Research Organisation of New Zealand
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Refers to Dept. of Textile and Fibre Technology unless otherwise specified.)
IWS	International Wool Secretariat
BWK	Bremer Woll-Kämmerei AG, Germany
FWS	Fairlie Wool Scour Ltd., Timaru
JWW	Jandakot Wool Washing Pty., Western Australia
CBF	Cross-Bred Fleece
P&ID	Piping and Instrumentation Diagram
PFD	Process Flow Diagram
UV	Ultra-Violet

1 INTRODUCTION

1.1 BACKGROUND

34% of the agricultural land in New Zealand is currently used for Sheep Farming (New Zealand Official Yearbook, 1998). In the 1999 – 2000 season this resulted in 193,000 tonnes of clean wool. Combined with the 438,000 tonnes per year wool production from Australia this represented approximately 46% of the world wool clip. At an average value of NZ$4.40 per kg, the New Zealand production of wool represented 4% of the country's total exports for the 1999 – 2000 year (WRONZ 2001).

Wool scouring is the process of taking freshly shorn wool and washing off the contaminants (natural, acquired and applied) to produce a value added product suitable for further processing such as spinning.

Natural impurities in the fleece consist primarily of wool grease and suint (sheep sweat salts) that are produced by the sheep.

- Wool grease is secreted from the sheep's skin and accumulates in the wool fibre as it grows. Wool grease is a mixture of fats and oils with a combined melting point of approximately 40°C. Wool grease can be emulsified in water by the addition of a detergent

- Suint is made up from a mixture of primarily potassium-based salts. It is excreted from the sweat glands of the sheep and dries onto the skin and wool fibres. Suint is highly soluble in water.

Acquired impurities are picked up from the animal's natural environment, and can be categorised as mineral or vegetable contaminants.

- Mineral contaminants include dirt, dust, sand and stones. These are usually quite straightforward to remove by washing.

- Vegetable matter (VM) caught in the animal's fleece commonly includes straw, grass, seedpods, pieces of plant tissue and twigs. Parasites such as ticks and blowfly maggots as well as faeces attached to the wool are generally defined as VM along with the true vegetable contaminants (TOPNZ 1992).

Applied impurities cover the range of farm chemicals such as sheep dip and fertilisers applied directly to the sheep or to the pasture upon which they are grazing. These generally only occur in trace quantities and can be very difficult to separate from the other contaminants.

1.2 THE SCOURING PROCESS

With the exception of occasional attempts to develop dry or organic solvent based cleaning systems (Baker *et al.* 1990), contaminants are mostly removed from the fleece by the use of aqueous wool scouring. Aqueous wool scouring uses gentle agitation in water with a combination of detergents, alkalis, acids, and sometimes hydrogen peroxide or other chemical additives to remove contaminants from the raw wool.

A modern wool scour consists of multiple hopper-shaped bowls arranged in series, which are operated as separate washing and rinsing sections. The wash section commonly uses 1 – 5 litres of fresh water per kilogram of greasy wool processed, while the rinse section typically uses water volumes which can range from 6 litres per kilogram of wool washed to more than 15 litres per kilogram.

Figure 1.1 Modern wool scouring line

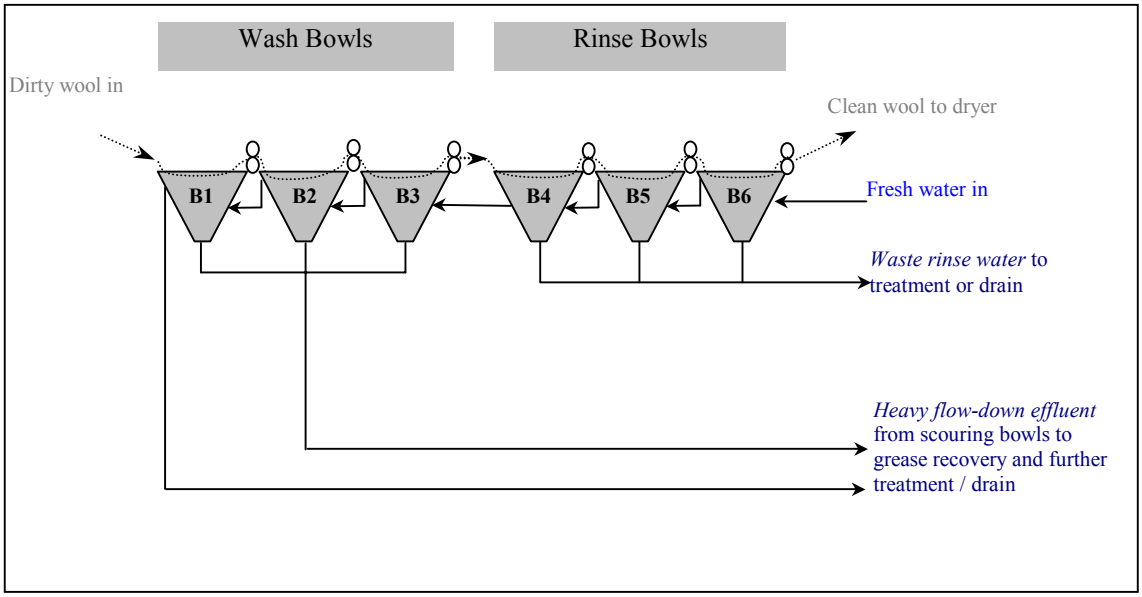


Figure 1.2 Conventional wool scour configuration

The wool is passed through squeeze presses after each bowl to prevent entrainment of water-borne contaminants from dirty bowls to cleaner ones, thus maintaining a counter current contacting of the wool and wash water. Squeeze pressing of the wool as it leaves the final rinse bowl also minimises the water loading in the wool being sent to the final dryer, thus significantly reducing the energy use of the overall process.

There are many adaptations of the described system, where the rinse and wash sections are alternated. For example one option currently in use is to operate B1 and B2 in Figure 1.2 as wash bowls, then use B3 as a rinse bowl followed by B4 as another wash bowl. B5 and B6 then act as the final rinse bowls (Christoe 2000a).

The key differences between a wash bowl and a rinse bowl are:

<u>Wash bowl</u>

- Contains detergent / surfactants
- Is run hot (50 – 60°C, dictated by the type of detergent used)
- Is operated at a high suspended solids level (up to 8 – 12% solids in bowl 1)
- Relatively low water use.

Rinse Bowl

- Contains minimal or no added detergents
- Either hot or cold water is used
- The water in the bowl is kept cleaner (seldom above 1.2% solids in bowl 4)
- A larger volume of water is generally used

Two of the most common alterations to the system include operation of the final rinse bowl (B6 in Figure 1.2) as a peroxide bowl, or operation of the first bowl as a suint bowl.

For the first option, the final bowl is isolated from the rest of the rinse system and run in batch mode with only enough water added to make up for losses through the squeeze press and periodic purging of solids build-up in the base of the hopper. The bowl is acidified by the addition of either formic or sulphuric acid and the contents held at 1 - 2% hydrogen peroxide concentration by continuous metered dosing of bulk peroxide. The key goal of this process is to improve the final product colour by using the peroxide to whiten the wool.

The second option of using Bowl 1 as a suint bowl, or as is also often done, adding an additional bowl to the front end of the process to be used as a suint bowl, is becoming increasingly common throughout the industry. The option of using an additional suint bowl is illustrated in Figure 1.3 below:

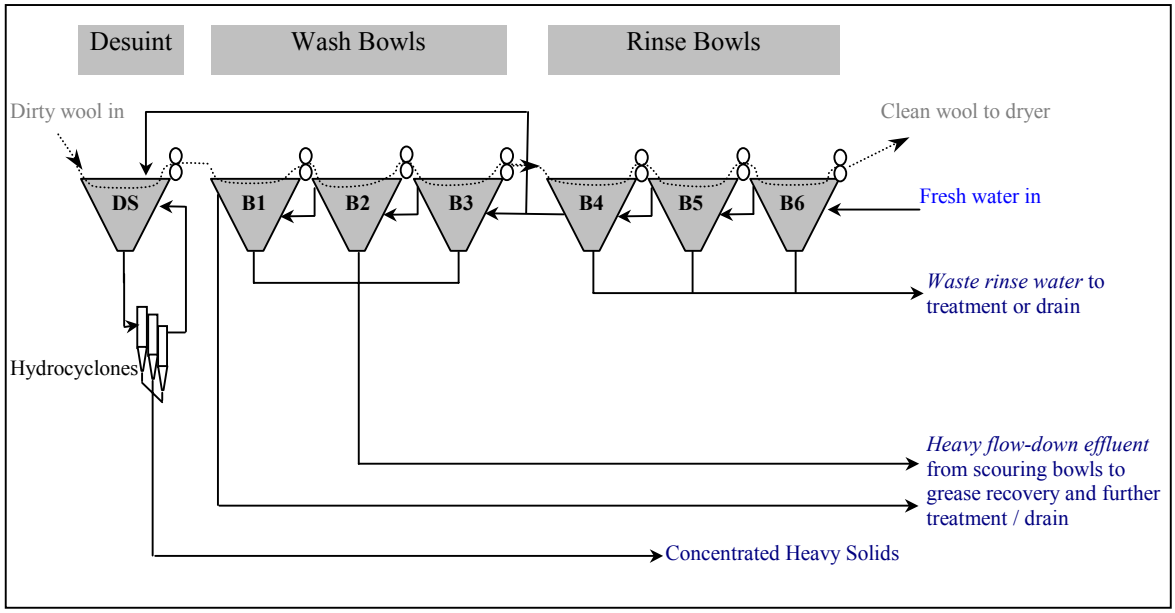


Figure 1.3 Use of an additional desuint bowl

The suint bowl is generally operated cold, and contains only a very small quantity of detergent. Enough detergent is used to promote complete wetting of the wool, without providing enough to emulsify the wool grease bound to the fibres. The purpose of these operating conditions is to allow the water-soluble suint and the dirt fraction to be removed in the suint bowl while leaving the wool grease on the wool for separate removal in the wash bowls.

This partitioning of contaminants allows recovery of dirt and wool grease from separate streams, as opposed to both being extracted from the Bowl 1 liquor as occurs in a conventional scouring set-up (Figure 1.2). The dirt is usually extracted from the effluent by a hydrocyclone bank in a recycle loop off the desuint bowl (as shown in Figure 1.3) while the grease is extracted from the Bowl 1 liquor by a series of disc-stack centrifuges operating in a recycle loop off the first wash bowl. By splitting the effluent streams in this manner, better removal efficiencies can be achieved for both the dirt and grease fractions (TOPNZ 1992), and component wear in the wool grease centrifuges due to dirt erosion (a major concern in the operation of this equipment) is significantly reduced. In a suint scouring system the suint solution from the first bowl is returned to the bowl after the solids have been removed. The subsequent high concentration of salts in the bowl combines with some of the wool grease to form soaps that aid in the washing process (Christoe 2000b).

Due to the high resale value of wool grease (also known as lanolin) recovered from wool scouring effluent, virtually all wool-scouring plants throughout the world operate some form of wool grease recovery from their wash bowl effluent. Whether it be for reduced water use, improved effluent quality, or just to decrease component wear in the wool grease centrifuges, installation of heavy solids recovery loops (on suint bowls or on Bowl 1 effluent prior to wool grease recovery) has also become prevalent throughout the industry.

The economical removal of the remaining contaminant fractions from this water once it has passed through the grease recovery process is a problem to which the current solution is far from optimal. Some currently available systems are able to meet the tightening environmental discharge constraints being placed upon them by regulatory authorities, and in one or two cases even supposedly provide ‘complete’ recycle of wash water (such plants boast that they simply do not have a ‘waste water to drain’ pipe). These systems however often prove expensive to the extent that they are not economically viable without external capital funding of the order of millions of dollars from the government or environmental authority that is imposing the discharge limitations upon them.

Current treatment systems used for contaminant removal from wool scouring effluent generally include combinations of:

- Gravity solids removal
- Wool grease recovery by centrifuge
- Coagulation / Flocculation
- Dissolved Air Flotation
- Anaerobic / Aerobic biological treatment.
- Membrane Filtration (ranging from micro-filtration to reverse osmosis)
- Evaporation

1.3 EFFLUENT CHARACTERISTICS

1.3.1 OVERVIEW

The two main effluent streams produced by an aqueous wool scour are rinse water (Figure 1.5) and heavy flow-down effluent (Figure 1.4). The rinse water is a high volume low strength waste stream while the heavy flow-down is generally a high strength, lower volume waste stream.

Figure 1.4 Heavy flow-down discharge to drain

Figure 1.5 Rinse water discharge to drain

Table 1.1 Typical effluent characteristics (after wool grease recovery)

Contaminant	Heavy Scour Effluent	Rinse Water
Biological Oxygen Demand BOD_5[mg/L]	9,800 – 50,000	200 – 1,000
Chemical Oxygen Demand COD [mg/L]	30,000 – 100,000	500 – 2,000
Total Suspended Solids TSS [mg/L]	20,000 – 60,000	100 – 700
Solvent Extractables SE* [mg/L]	1,000 – 2,000	50 – 1,500

**SE is made up of detergent and wool grease.*

As shown by the data ranges in Table 1.1, there is commonly a large spread in effluent quality between different wool scours. This can be attributed to 4 main factors:

- Wool Type being processed
- Yield of the wool being processed ($kg_{clean\ wool}$ / $kg_{greasy\ wool}$)
- Local cost of supply and disposal of water
- Mode of operation of the wool scour

The first two of these factors are often tied together. For example, high fibre diameter New Zealand cross-bred fleece wool will commonly show a yield of around 80% (the raw wool off the sheep is 80% wool and 20% other contaminants such as dirt, wool grease and vegetable matter) and subsequently produces a relatively low level of contamination. Fine West Australian Merino wool however can display yields as low as 45%, i.e. over half the weight of the dirty wool fed to the scour is dirt and other contaminants which are removed in the effluent water. Needless to say, the strength of effluent from plants treating this type of wool is significantly higher than that of the previous example.

These factors often combine to give extreme examples of effluent quality. One such case is an Australian Scour that has a very high cost of water and is employed only to process extremely low yielding, fine micron wool. In this plant the volume of rinse water used is often as low as that used in the wash bowls of the scour, and the effluent produced is almost as dirty. At the other end of the scale is a New Zealand scour with extremely low water cost, which typically processes very high yielding wool. In this case up to 12 times as much rinse water is used as wash water, and the subsequent concentration of contaminants in the rinse water effluent is only marginally higher than that of the clean water entering the process.

1.3.2 DIRT / SOLIDS

This category of material generally covers the range of solid contaminants with specific gravities of greater than 1.0. The composition and characteristics of the inorganic matter entrained in the fleece depends primarily upon the environment in which the sheep was grown, and the type of wool in which it is contained. For example, coarse crossbred fleece wool from New Zealand contains very few solids and those which do occur tend to be easily removed, whereas low micron West Australian merino fleece tends to be heavily laden with fine red sand that is extremely difficult to remove in the scouring process. Coulter counter analysis has revealed that wool scour liquor has a bimodal particle size distribution with one peak below 1μm, and one at 5 – 10μm. It has been concluded that the finer particles are from the weathered tips of the fleece, while the larger course particles are more deeply held near the base of the fleece (Worth *et al.* 1993).

Dirt and solid contaminant is primarily removed by agitation of the wool in the wash bowls and movement of the wool through the nip of the squeeze presses (Figure 1.6). The latter is considered a significant contributing factor due to the high volume of water, which is forced

through the wool entering the nip, thus entraining and removing dirt and other contaminants loosely bound to the fibres (TOPNZ 1992).

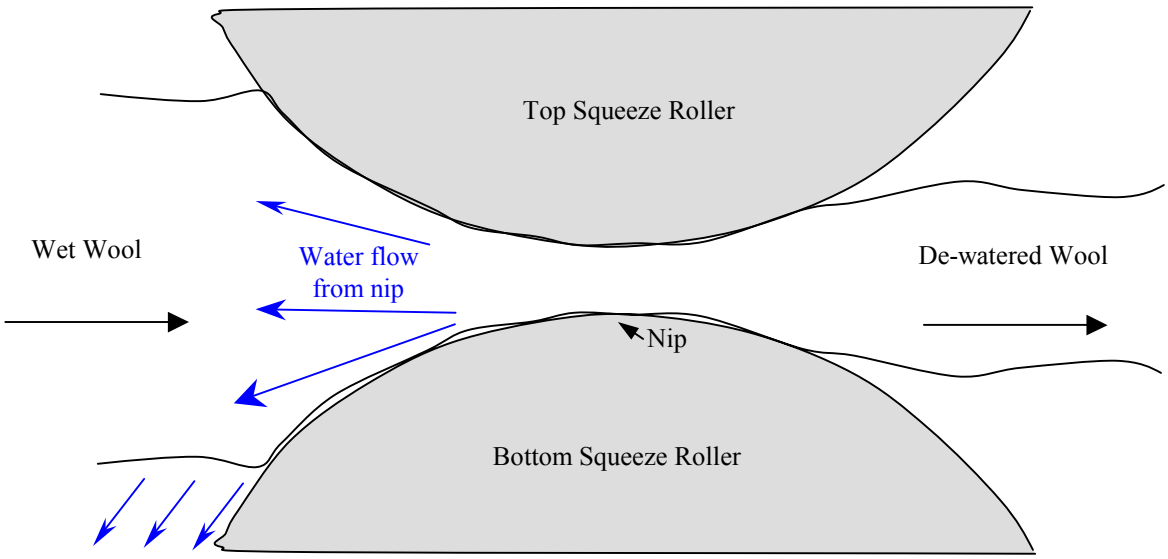


Figure 1.6 The squeeze pressing of wool

Due to the counter-current nature of the scouring process, Bowl 1 has the highest solids content, which is usually maintained between 7 - 12% w/w solids. This is where the bulk of the waste water from the wash section is drawn off.

Virtually all the methods utilised for removal of solids from the heavy wash effluent are based on the following principles:

- Gravity Settling
- Centrifugal Separation (Cyclones or Decanter Centrifuges)
- Dissolved Air Flotation
- Evaporation

In any of the first three options, addition of chemical coagulant (e.g. alum) and or flocculent (e.g. polyacrylamide) is commonly practised to enhance removal efficiencies.

Until recently, the predominant treatment systems for dirt removal had been heavy solids tanks (gravity settling) and hydrocyclones with average removal efficiencies in the range of 10 – 20% of the total suspended solids. Under pre-existing effluent discharge constraints

(particularly in New Zealand) there has been little economic driving force for any more complete clean up of the effluent than this. Indeed, in most wool scours prior to circa 1980, the only reason that any solids removal was carried out at all was to remove large abrasive particles from the effluent stream prior to wool grease recovery, thus minimising abrasive wear of the wool grease recovery centrifuges (Stewart 1974).

The end of the 20th Century however, has brought a general trend towards local government and international regulatory bodies (such as the European Union) imposing tight mandatory limits on the maximum level of contamination that can be discharged in any given industrial effluent stream (Brach *et al.* 1990). Increasing discharge fees, which are generally negotiated on a plant by plant basis with the local authority whose water ways / effluent treatment plants receive the effluent stream, are also providing an incentive for achieving maximum possible contaminant removal before the effluent leaves the site where it is generated.

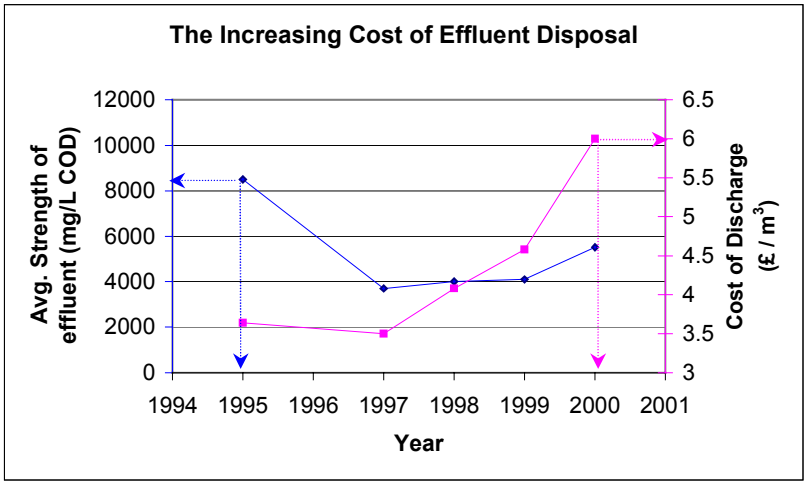


Figure 1.7 Cost of effluent discharge for one U.K. scour over the last 5 years (Confidential Commercial Source)

Figure 1.7 shows a trend in effluent discharge cost typical throughout the UK and Europe and which is becoming more common in the rest of the world. Despite a 40% improvement in quality of effluent discharged from the site over the last 5 years, the cost of discharging this effluent to the local treatment authority has increased by approximately 70%. This pattern is rapidly becoming one of the key issues determining the viability of aqueous wool scouring operations. "Clean up your effluent, or close the doors" is becoming a common ultimatum.

1.3.3 WOOL GREASE

Also known as wool wax or Lanolin (derived from 'Lana': Latin for wool; and 'oleum' meaning oil) wool grease is both the most valuable and arguably the most difficult to deal with of the three main contaminants of wool scouring effluent.

30 jobs to go when plant closes

WELLINGTON — Almost 30 jobs will go when Lower Hutt wool scouring company Seaview Wools closes its doors later this month in the face of rising effluent charges.

General manager Alan Husheer said last night the company, which employed 27 staff in total, faced extra costs imposed by the Hutt City Council of $1900 a day for treatment and discharge.

He said that would take the business' operating costs to around $500,000 a year, making them uncompetitive. — NZPA

Page 2 The Timaru Herald Saturday August 4 2001

Figure 1.8 Newspaper clipping from 'The Timaru Herald', Saturday August 4, 2001.

1.3.3.1 Chemical Composition of Wool Grease

Wool Grease is a natural substance excreted from the sebaceous gland attached to the root of each wool fibre in the basal layer of the sheep's skin (Figure 1.9).

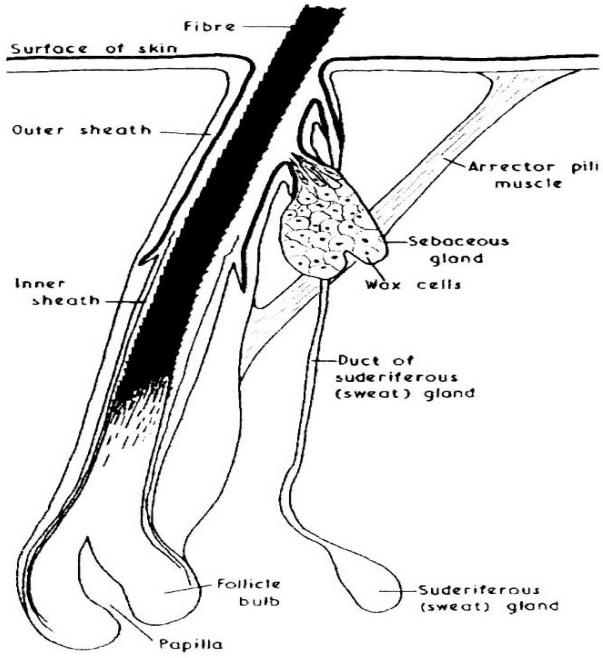


Figure 1.9 Dermal detail of a wool follicle (WRONZ 2001)

The wax excretion forms a hydrophobic coating on the fibre, protecting it from the elements.

By chemical definition, the absence of glycerol in this oily excretion makes it a wax. Wool Wax is also becoming a favoured terminology in industry due to the perceived value of a 'wax' as opposed to a 'grease' (which is often associated with waste and pollution in the wool industry).

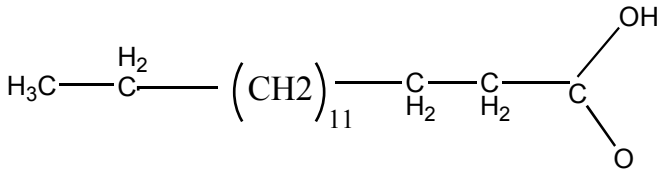
The wax itself is a complex mixture of naturally occurring esters of water, insoluble alcohols and higher fatty acids. A collection of typical physical properties of the wax, compiled by Truter (Truter 1956), is as below:

Table 1.2 Physical properties of wool wax

Colour		yellow to pale brown
Specific Gravity (15°C)		0.94 –0.97
Refractive index (40°C)		1.48
Melting Point		35 – 40°C
Free Acid content		4 – 10%
Free Alcohol content		1 – 3%
Iodine Value (wijs)		15 – 30
Sponification Value		95 – 120
Molecular Weight (Rast; in salol)		790 –880
Proportion of fatty acids		50 – 55%
Proportion of alcohols		45 – 50%
Acids:	Melting point	40 – 45°C
	Iodine Value (wijs)	10 – 20
	Mean molecular weight	330 g/mol
Alcohols	Melting point	55 – 65°C
	Iodine Value (wijs)	40 – 50
	(Dam)	70 – 80
	Mean molecular weight	370 g/mol

Isolation of specific esters is extremely difficult and seldom attempted (Truter 1956) but detailed analysis has been carried out on the free acids and alcohols from which the esters are formed. In 1954 a large range of wool wax acids were identified and found to fall into 4 distinct series: normal (Figure 1.10a), *iso*- (Figure 1.10b) *anteiso*- (Figure 1.10c), and *hydroxy*-acids (Figure 1.10d). Examples of each series are given below:

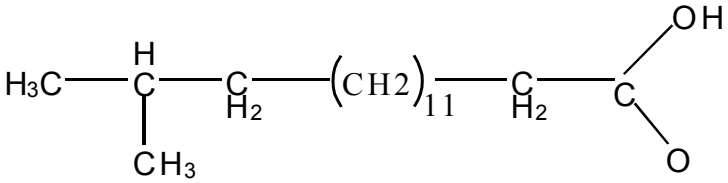
a)



n-hexadecanoic acid

(palmitic acid)

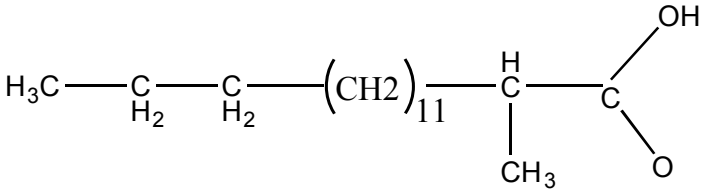
b)



iso-hexadecanoic acid

(*iso*-palmitic acid)

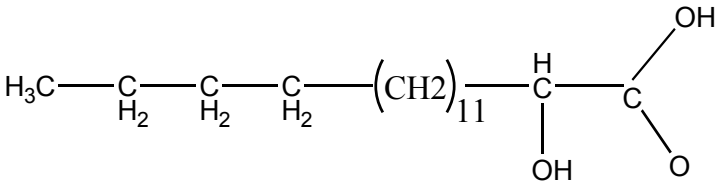
c)



14-methylhexadecanoic acid

(*anteiso*-palmitic acid)

d)



2-hydroxyhexadecanoic acid

(α-hydroxy-palmitic acid)

Figure 1.10 Structure of wool wax acids

Table 1.3 Acidic fraction of wool wax

Acidic Fraction	Approximate Content (% of total acids)
n-Acids	7
iso-Acids	22
anteiso-Acids	29
α-Hydroxy-*n*-acids	25
α -Hydroxy-*iso*-acids	3
Total	**86**
Residual (speculated to be mostly saturated acids)	14

The free alcohol component is primarily made up of three groups: aliphatic alcohols, sterols, and isocholesterol. A summary of these groups and their constituents is given in Table 1.4.

Table 1.4 Alcoholic fraction of wool wax - *After Truter (Truter 1956)*

Alcoholic Fraction	Approximate Content (% of total alcohols)
Aliphatic alcohols	
n-Alcohols	4
iso-Alcohols	6
anteiso-Alcohols	7
n-Alkan-1, 2-diols	0.5
iso- Alkan-1, 2-diols	3
Sterols	28
Isocholoresterol	27
Hydrocarbons	1
Total	**78**
Unidentified Residue	22

From a practical perspective, the wool grease dispersed in scour effluent consists of two main fractions, typically referred to as ‘oxidised’ and ‘unoxidised’ wool grease. The oxidised wool grease has been shown to be associated with the tip of the wool staple where the grease is exposed to the air and the external environment while the unoxidised fraction has been shown to be more predominant at the base and centre of the wool staple (Brooks 1984). It is generally agreed that the oxidised fraction has a higher density than the unoxidised, but the actual values reported in various works vary widely. For example, Brooks and Baumann

(Brooks *et al.* 1983) give values of 924.8 and 995.4 kg/m^3 at 60°C for unoxidised and oxidised wool grease respectively, while McCracken and Chaikin (McCracken *et al.* 1971) attribute densities of 905 and 924 kg/m^3 at 60°C respectively to the same fractions. McCracken and Chaikin also go on to identify a third fraction, the 'surface active' fraction to which they attribute a density of 979 kg/m^3 at 60°C.

As the density of water at 60°C is 983 kg/m^3 (Rogers *et al.* 1995), and the bulk density of scour liquor (although highly variable) was measured as 980 kg/m^3 at 60°C during the above density determinations (McCracken *et al.* 1971), it becomes obvious that the surface active and, if Brooks and Baumann are to believed, unoxidised fractions of the wool grease would be extremely difficult to separate from the aqueous and sludge phases in a gravity disc centrifuge.

Both of the investigations discussed (McCracken *et al.* 1971; Brooks *et al.* 1983) developed linear correlations between the methanol extractable fraction of the total wool grease and the oxidised fraction. McCracken and Chaikin backed this up by confirming a linear relationship between the methanol-insoluable fraction of the wool grease and the fraction of the wool grease that could be recovered by gravity centrifuge.

1.3.3.2 Wool Grease Recovery

Due to its low specific gravity, unoxidised wool wax is most commonly recovered by passing the scour effluent through a centrifuge. At present, stacked disc centrifuges similar to those employed in the dairy industry are used in either a 2 or 3 stage separation and purification process.

The main processes used throughout the world for wool grease recovery involve some combination of thermal cracking and centrifuging. Solvent extraction methods have been extensively developed and typically give a very high quality product (Truter 1956), but these technologies have never gained widespread use.

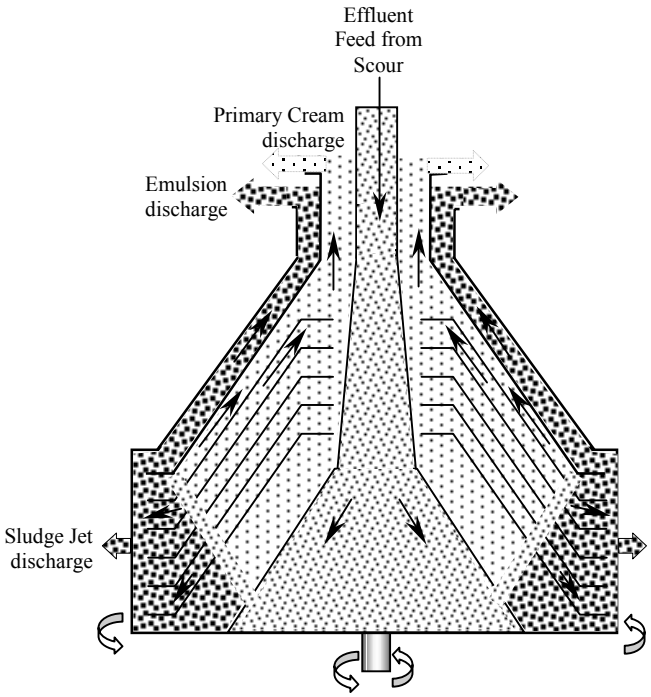


Figure 1.11 Primary centrifuge

1.3.3.3 Single-Stage Wool Grease Recovery

Scour effluent heated to at least 64°C is fed from above into the centre section of the primary centrifuge as shown in Figure 1.11. Inside the centrifuge the effluent flows into the stack of cone shaped discs, which rotate at approximately 6000rpm. In the disc stack the lighter wool grease flows upwards between the discs towards the centre of the bowl where it is discharged as primary cream. A second emulsion phase flows downwards between the discs due to its higher density, from where it flows up the walls of the outer bowl and is also discharged at the top of the centrifuge. Any dirt and heavy solids in the feed are also carried downwards between the discs but, due to having higher density than the aqueous emulsion phase, do not flow up the walls with the emulsion phase and are continuously discharged through jets in the bottom of the bowl wall.

The primary cream is then fed into a thermal-cracking tank where it is held for in excess of five hours at approximately 90°C. Over this period the cream splits into three distinct phases (see Figure 1.12).

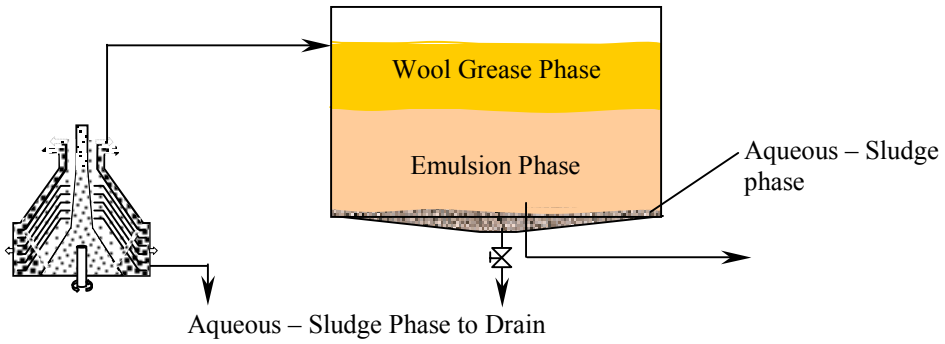


Figure 1.12 Single-stage wool wax recovery.

After the solution has been given time to separate, the heavy aqueous phase is drawn off the bottom of the tank to drain, the emulsion phase is recycled to the centrifuge and then the wool grease floating in the top of the tank is drawn off into drums. Due to the rising value of recovered wool grease and mounting restrictions on effluent discharges, single stage wool grease recovery is no longer used in the main stream scouring industry.

1.3.3.4 Two-Stage Wool Grease Recovery

In a two-stage system, primary centrifuges and thermal cracking tanks are again used, but this time the cream and emulsion from the cracking tank is fed to a bank of secondary centrifuges for further purification. In a two-stage system the cream from the primary centrifuges is around 60 – 80% wool wax. The product from the secondary centrifuges is typically in excess of 99% pure. (TOPNZ 1992)

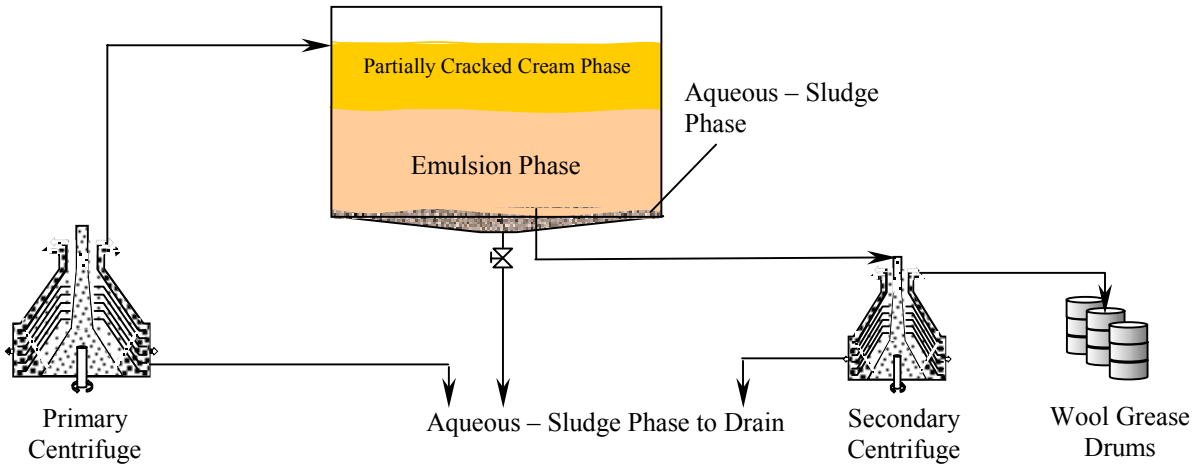


Figure 1.13 Two-stage wool wax recovery

The escalating value of the recovered wool grease (Figure 1.14) has led to two-stage wool grease recovery almost entirely replacing single-stage plants over the last ten years. Single stage plants were found to have great difficulty with, or even fail altogether, when handling 'hard to separate' wool grease emulsions such as the sulphite stabilised effluent produced from slipe wool washing, or effluent from fine Australian merino wool (TOPNZ 1992).

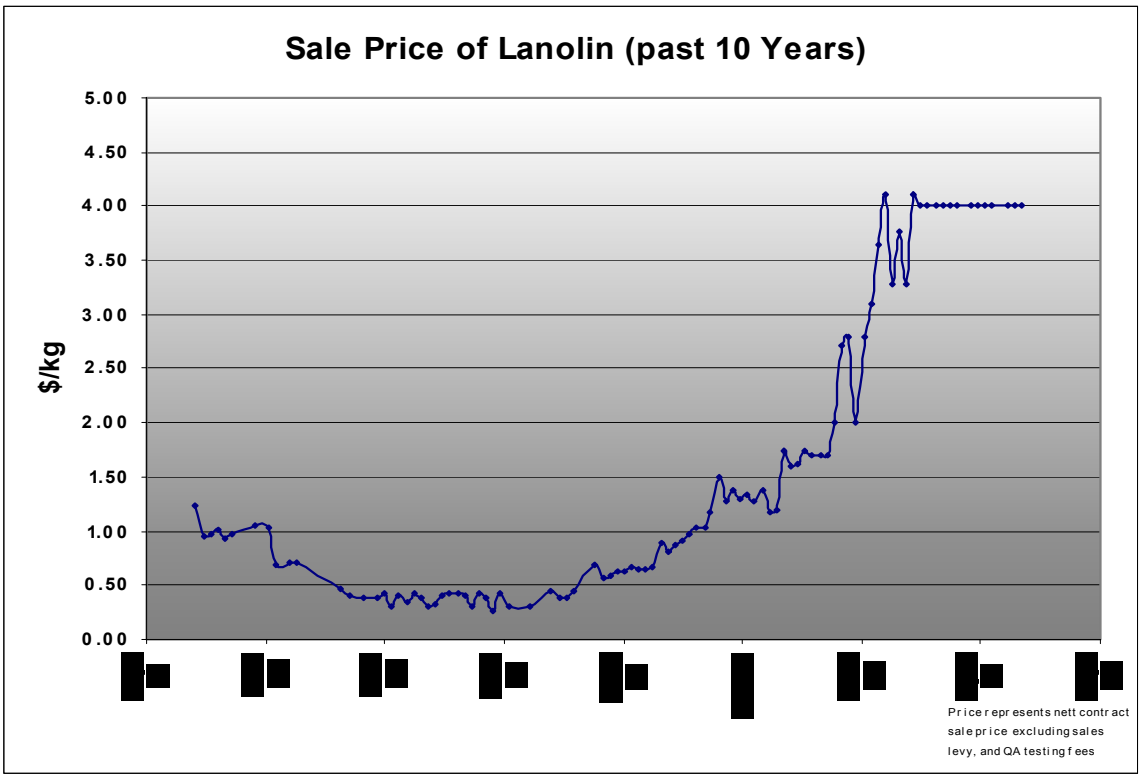


Figure 1.14 Lanolin (wool grease) price 1992 – 2002 (Confidential Commercial Source)

1.3.3.5 Three-Stage Wool Grease Recovery

Towards the end of the 1990s three-stage wool grease recovery began to gain favour as wool grease prices continued to increase (Figure 1.14).

In a three-stage system a greater overall proportion of the wool grease is recovered from the effluent by the primary centrifuges. The resultant primary cream however is typically only 10 – 20% grease.

This high volume low strength primary cream is then thermally cracked and passed through the secondary centrifuge at approximately 90°C resulting in a secondary cream containing 70 – 80% wool grease.

The cream from the secondary centrifuge, still at 90°C, is then passed to a purifying centrifuge where it is mixed with clean hot water (which aids in washing impurities from the grease) and is then separated to produce wool grease with purity in excess of 99%.

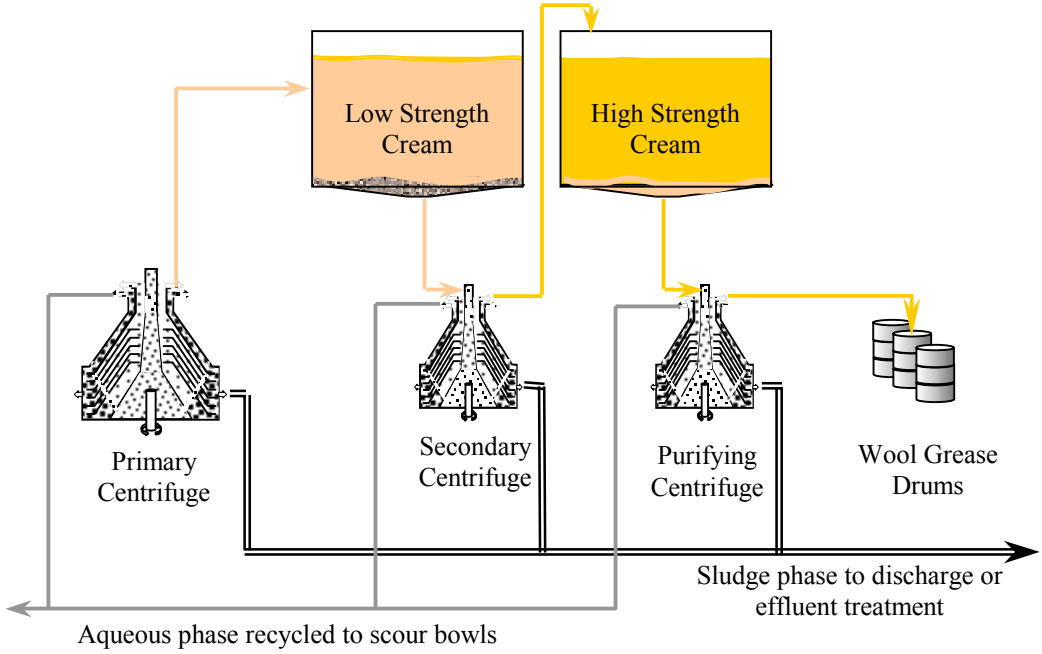


Figure 1.15 Three-stage wool grease recovery

Among a multitude of other uses, the raw wool grease has traditionally been used as an anti-corrosive coating and as a leather processing aid, while refined lanolin is more often used as a base for pharmaceutical and cosmetic products (Stewart 1988).

1.3.4 SUINT

The term suint typically covers the entire range of water-soluble salts contained in the wool fleece. Suint is primarily made up of potassium based fatty acid salts and smaller amounts of sulphates, phosphates and nitrogenous compounds. Suint originates from sheep sweat which, when dried, leaves the salts dissolved in the sweat attached to the fibres of the fleece. Suint salts are responsible for most of the distinctive odour of a greasy (unclean) sheep fleece.

On average New Zealand crossbred wool contains around 8% suint by weight, while Australian merino will typically contain around 6% suint by weight (Truter 1956).

As the suint salts tend to be highly soluble in water, little effort is required to remove them from the fleece during aqueous scouring. Processes such as 'suint scouring' involve the use of a concentrated suint solution in one or more of the wash bowls to aid in cleansing the wool.

This has two main advantages:

1) When suint combines with wool grease in solution it forms a slight soapiness, thus helping to clean the wool.

2) The water – suint solution has a pH of 7.5 – 8.0. In this pH range there is less chance of damaging the wool than in the traditional Soda-soap scouring process where Sodium alkaline soaps are added to the bowls.

Due to its high solubility in water, the final removal of suint from the wastewater requires the highest level of treatment of all contaminants. Suint removal systems generally involve evaporation, reverse osmosis or both and are preferably used after most other contaminants such as wool grease and dirt have been removed. The processes required for suint removal represent such a high capital and ongoing operating and maintenance investment that few installations around the world remove suint from their effluent prior to discharge.

As suint is high in potassium and organic nutrients (Table 1.5), the concentrate from an evaporation process, used after grease and dirt have been removed, is a concentrated renewable organic fertiliser suitable for addition to pasture via irrigation systems (Kroening 2002).

A typical breakdown of a concentrated suint solution is given below:

Table 1.5 Breakdown of a typical concentrated suint solution (Kroening 2002)

	Suint content (mg/ml) CFB Suint
Total Nitrogen	13.2
Available Nitrogen	2.2
Potassium	89.7
Phosphorus	0.9
Chloride	73.6
Copper (Cu)	0.007
Chromium (Cr)	0.004
Nickel (Ni)	0.005
Zinc (Zn)	0.016
Cadmium (Cd)	0.0002
Lead (Pb)	0.001

1.4 AIMS AND OBJECTIVES OF THE INVESTIGATION

The primary goal of this investigation was to develop and evaluate a biological system for the treatment of heavy wool scouring effluent that had been pre-treated by the proprietary Sirolan CF Chemical Flocculation system.

Should the biological process prove capable of treating this effluent to a standard where the process becomes an economical alternative to treatment systems currently available on the market, detailed design of a full-scale system will be carried out.

Intermediate objectives of the investigation included:

- Evaluate and optimise the effectiveness of the Sirolan CF Pre-treatment system
- Validate initial Australian CSIRO performance results (Bateup *et al.* 1996) under harsher New Zealand operating conditions
- Verify and optimise the biological pH neutralisation observed by the CSIRO
- Determine whether the biological system follows standard Monod style growth kinetics
- Qualitatively evaluate the biomass sludge formed in the biological reactor for properties such as floc formation and subsequent gravity settling.
- Evaluate the effect of scale up on the effectiveness of the biological reactor
- Evaluate the effect of different reactor configurations (e.g. multiple tanks operating in series versus one large continuously mixed reactor tank) on the effectiveness of the biological process
- Verify the operation of the process at full scale at an operational wool scour

2 REVIEW OF RELEVANT CURRENT INDUSTRIAL EFFLUENT TREATMENT PROCESSES

2.1 BIOLOGICAL SYSTEMS

The use of supplemental aeration to treat sewerage dates back to the 19th Century. In 1914 Arden and Lockett in England pioneered the process of recycling the flocculated microbial sludge from this process back to the feed of the aerobic process, thus developing the first activated sludge process (Orhon *et al.* 1994) pp 1 – 3.

Although the key process remains the same today, many advances have been made by modifying parts of the process to suit specific applications (such as denitrification) or to solve particular process problems (primarily sludge bulking).

One such example is the growing use of plug flow reactors (e.g. oxidation ditches) to treat readily degradable effluents, which would typically suffer from filamentous bulking in a complete mix reactor system. These systems have been operating effectively since 1953, when they were first used in Holland. Characteristics of the system are:

- Reduced Bulking Problems (due to concentration gradient)
- Performance Stability
- High Quality Nitrified Effluent
- Minimised Sludge Production
- Highly mineralised sludge (suitable for land application)
  (Eckenfelder 1992)

Tapered aeration is typically used in these systems such that most of the aeration is applied at the feed end of the plug flow reactor where the substrate concentration is highest, tapering off to minimum aeration at the discharge end where the minimum level of substrate digestion is encountered.

Modern processes are usually optimised in this or similar ways to achieve efficiency of oxygen utilisation and removal of particular effluent components or nutrients. The most common example of the latter case is the growing use of Biological Nutrient Removal (BNR) in both industrial and municipal waste treatment plants.

2.1.1 BIOLOGICAL NUTRIENT REMOVAL

Many regulatory authorities are realising that they cannot control the eutrophication and oxygen depletion impact of waste streams discharged to natural waterways based on the traditional parameters of BOD_5 or COD discharge alone.

Randall *et al* (Randall *et al.* 1992) give the following reasoning for limiting the discharge of nutrients into waterways:

> "The potential impact of discharged nutrients on the oxygen resources of receiving waterways can best be illustrated by looking at the amounts of organic matter that can be generated by the nutrients compared to the amount of organic matter in untreated sewerage. The COD of raw sewerage in the United States is typically about 400mg/L, whereas the phosphorus content is 6 to 10mg/L, depending on whether or not a phosphate detergent ban is in place, and the nitrogen content is 30 to 40mg/L. If one kilogram of phosphorus was completely assimilated by algae and used to manufacture new biomass from photosynthesis and inorganic elements, biomass of 111 kilograms with a COD of 138 kilograms would be produced, assuming algal composition can be represented by $C_{106}H_{263}O_{110}N_{16}P$. Thus, the discharge of 6mg/L of phosphorus could potentially result in COD production equivalent to 828mg/L, or more than double the COD of the organic matter in the untreated sewerage."

This subsequent COD loading is primarily biodegradable, so as the algal mass dies and is degraded, the oxygen uptake in the receiving waterway accelerates. Randall goes on to give a similar example for a case where nitrogen is the nutrient that limits organic growth. In this case, by the same process 30mg/L of nitrogen discharge results in the production of biomass with a COD of 600mg/L. In either of these cases, the natural 'background' concentration of the nutrient in the waterway under examination must be limiting for biological growth. If the nutrient being added is not that which is limiting biological growth, the impact of this nutrient addition on the eutrophication of the waterway will be minimal. Phosphorus is generally considered to be a growth-limiting nutrient in fresh water environments due to the high level of this element required for biological growth, and the high level of nitrate runoff into these waterways from farmland (Quinn *et al.* 2002).

In order to achieve biological nutrient removal one or more un-aerated zones must be introduced into the activated sludge system, and the return activated sludge from the secondary clarifier should be recycled to the first of these un-aerated zones. More

specifically, an anoxic zone is used for biological nitrogen removal and an anaerobic zone is used for biological phosphorus removal.

2.1.1.1 Biological Nitrogen Removal

In this system the biological processes of nitrification and denitrification are used to convert nitrogenous compounds to nitrogen gas, which is stripped from the solution by the aeration in the aerobic reactor. In order to achieve this, ammonia is oxidised to nitrite then nitrate by *Nitrosomonas* and *Nitrobacter* respectively in the aerated vessel (nitrification). The nitrate is then fed to an un-aerated zone where, in the absence of oxygen, it is utilised by a wide range of heterotrophic organisms as the terminal electron acceptor in microbial respiration (Stensel 2001). The later part of this process results in the production of molecular nitrogen, which is then stripped off as nitrogen gas in the aerobic zone. The simplest implementation of this process with a continuous mix activated sludge process is illustrated in Figure 2.1.

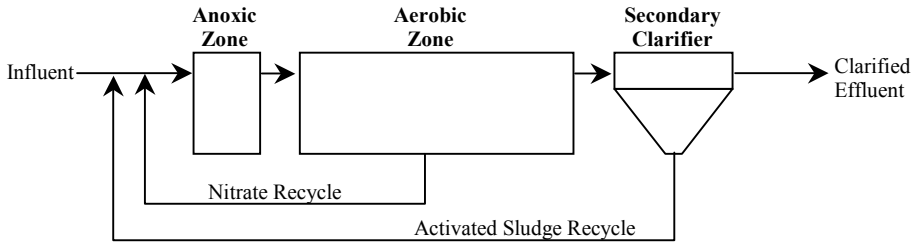


Figure 2.1 Simple biological nitrogen removal system

Alternatively, the same result can be achieved in a sequencing batch reactor by simply turning the aeration device off for a given amount of time to achieve an anoxic stage.

The process illustrated in Figure 2.1 (often described as the Modified Ludzack-Ettinger process) is seldom able to achieve results of less than 5mg/L total nitrogen in the clarified effluent when treating domestic sewerage (Randall *et al.* 1992). Therefore a number of adaptations and extensions of this process have been made. The Bardenpho process (Figure 2.2) is reported to be able to produce an effluent of less than 3.0mg/L total nitrogen from the same effluent (Randall *et al.* 1992).

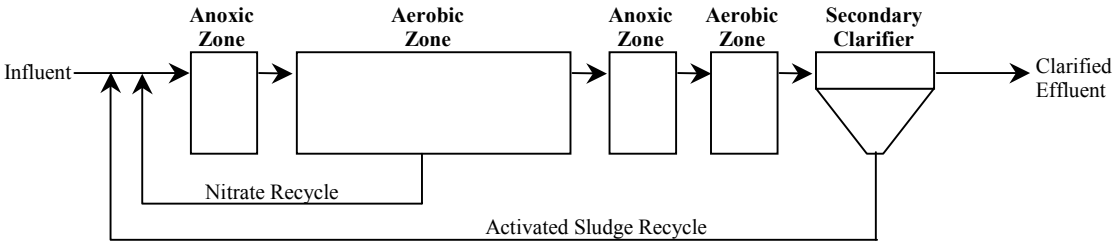


Figure 2.2 Bardenpho process for improved biological nitrogen removal

2.1.1.2 Biological Phosphorous Removal

The effective removal of phosphate in the activated sludge system is a somewhat more complicated process. The process involves the conversion of short chain fatty acids to poly-β-hydroxybuterate (PHB) under anaerobic conditions (Randall *et al.* 1992). The PHB is then stored inside the cells until the organisms encounter aerobic conditions where the PHB is used as an energy source for the uptake of orthophosphate from the effluent. The orthophosphate is converted into polyphosphate, which is stored for use in the cell.

Traditionally one of the biggest hindrances to biological phosphate removal is the presence of nitrate in the anaerobic zone (Ekama *et al.* 1999; Stevens *et al.* 1999). When nitrate is present, many organisms preferentially utilise this as a terminal electron acceptor in the metabolism of volatile fatty acids. This oxidation pathway rapidly reduces the available level of volatile fatty acids without resulting in the production of PHB. This subsequently limits the amount of energy available for uptake of orthophosphate from the effluent in the aerobic reactor.

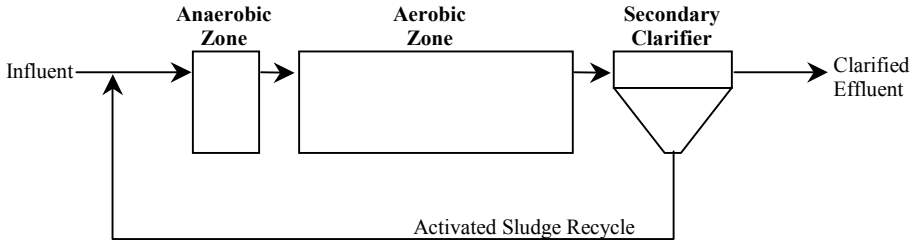


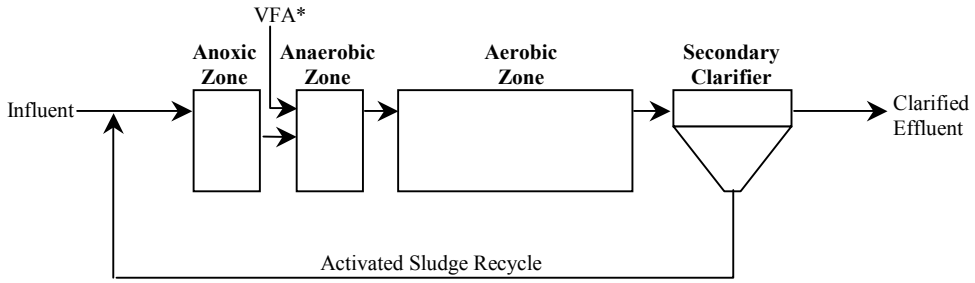
Figure 2.3 Simple 2-stage biological phosphorus removal system

Although recent works have verified that some organisms responsible for phosphate removal are also capable of denitrification (Stevens *et al.* 1999), it is generally accepted that this is

seldom the case. The two main approaches taken to optimise biological phosphorus removal are:

- Reduce the nitrate content fed to the anaerobic zone (e.g. by passing the recycle activated sludge through an anoxic zone to remove nitrates prior to mixing with the effluent feed)
- Maximise the level of volatile fatty acids such that sufficient is available for both denitrification and complete orthophosphate uptake to take place (Elmendorf *et al.* 1994).

The later is often achieved with a pre-fermenter in which primary sewerage solids are fermented and the volatile fatty acids rich supernatant is added to the anaerobic stage of the phosphorus removal system. A typical example of a process which implements both of these options is the patented VIPR (Volatile acid Induced Phosphorus Removal) process, which only utilises sufficient denitrification to protect the phosphorus removal system (Elmendorf *et al.* 1994).



*VFA = Supplemental Volatile Fatty Acids from Pre-Fermenter

Figure 2.4 VIPR process for advanced phosphorus removal

In the design of a biological nutrient removal plant both nitrogen and phosphorus removal are targeted. In these cases the process flow sheet would typically resemble Figure 2.5 with the possible inclusion of modifications such as those depicted in Figure 2.2 and Figure 2.4.

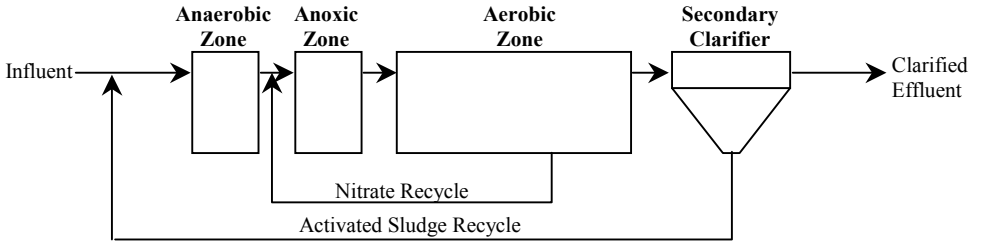


Figure 2.5 Simple 3-stage biological nutrient removal system

2.1.2 MEMBRANE BIOREACTORS (MBRS)

Significant technical and economic advances have been made in the last 10 years in the use of membrane bioreactors for the treatment of both municipal and high strength industrial effluents.

One of the key factors that has caused membrane bioreactors to gain favour recently is the decreasing cost of membrane replacement. This is illustrated by Churchouse and Wildgoose (Churchouse *et al.* 1999) in Figure 2.6 below:

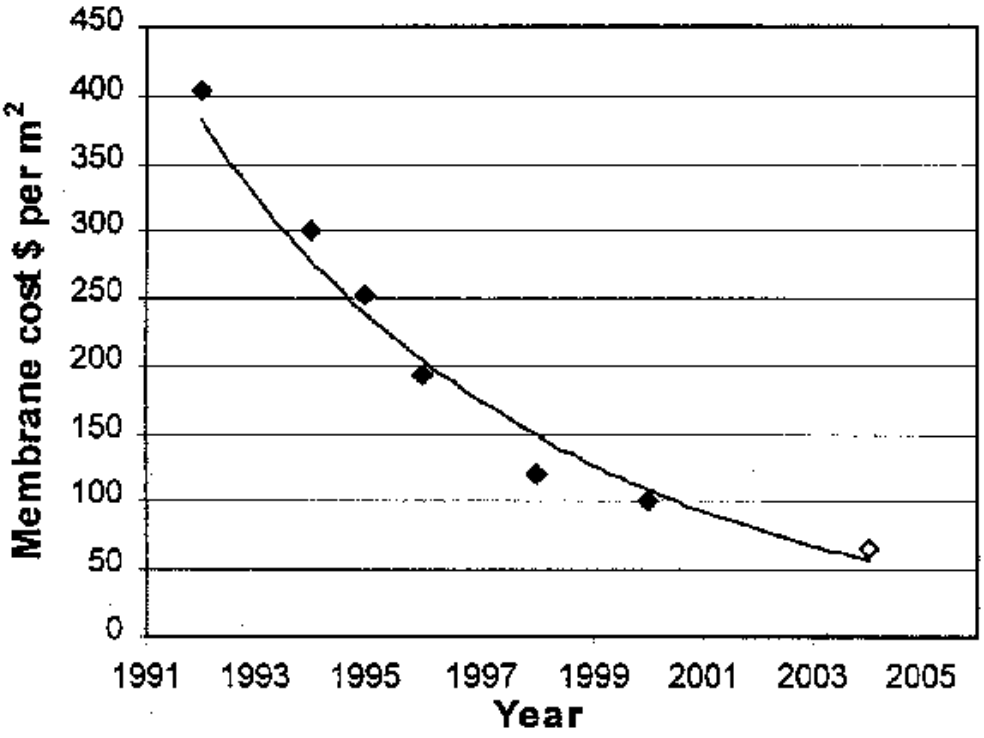


Figure 2.6 Reduction in actual and projected membrane replacement costs (1999 $US / per m^2) After (Churchouse *et al.* 1999)

The membrane bioreactors gaining popular use in the field of industrial effluent treatment are primarily adaptations of the activated sludge process where micro- or ultra-filtration are used in the place of gravity settling for the purpose of sludge recycle and product clarification.

Most of the commercial facilities in operation today utilise one of the two following membrane systems:

- Hollow fibre or plate and frame membranes suspended within the aerated activated sludge reactor.
- Cross flow membranes located in a module outside the biological reactor, through which the mixed liquor is pumped at elevated pressure.

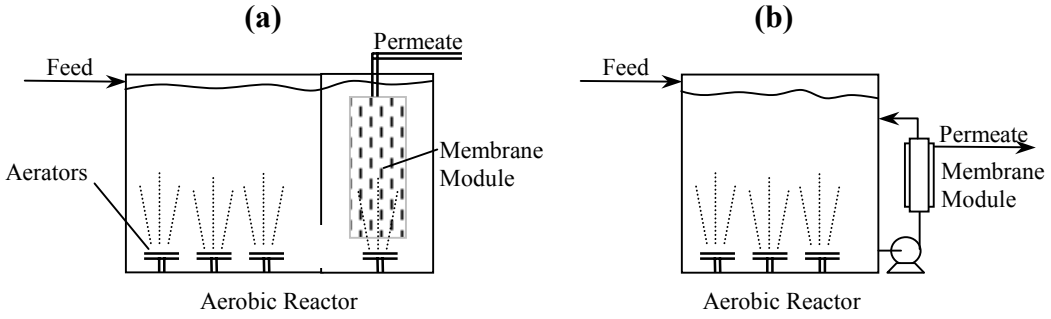


Figure 2.7 Typical membrane bioreactor configurations a) suspended membranes b) cross-flow module

Bennett (Bennett circa 2000) describes the first fully automated commercial application of a membrane bioreactor for treatment of industrial waste in the UK. This application consists of an activated sludge plant utilising Zenon ZeeWeed™ tubular microfiltration membranes suspended in the aerated bioreactor tank (as in Figure 2.7a). The effluent being treated is mixed wool scouring effluent pre-treated by dissolved air flotation and has a COD of 3,500 – 5,000mg/L, which is less than one third that of wool scour heavy flow-down effluent pre-treated by chemical flocculation. At the time Bennett's results were published he concluded that the process had not been operating for long enough to evaluate operating costs or process stability. Personal communication with the wool scour in question has revealed that at the feed strength given, the membrane bioreactor is operating at the limit of its process suitability, and often becomes unstable. This conclusion has also been substantiated in research by Rossenberger *et al* (Rosenberger *et al.* 2000) who compared the operation of the Zenon submerged hollow fibre membrane bioreactor to that of a Stork cross-flow type membrane bioreactor. The Zenon system was suitable for treatment of effluent of approximately 750mg/L COD, while the cross-flow system proved effective and reliable at treating a synthetic industrial effluent of up to 4000mg/L COD.

In this study Rossenberber *et al* carried out an extensive study of the microbial fauna present in the bioreactors under varying process conditions. High concentrations of well-flocculated, dispersed growth, and filamentous micro-organisms were all encountered during various phases of operation. Unlike the conventional activated sludge process, none of these

microbial conditions expressed negative influences on the effluent quality or operational stability of the reactor.

Male and Pretoruis (Male *et al.* 2001) carried out an investigation into the use of high-pressure membrane bioreactors for the treatment of high strength industrial waste (COD ~ 11,500mg/L), which exhibited biological growth consistent with substrate inhibition kinetics. The laboratory scale membrane bioreactor operating at a pressure of 3-bar provided more stable operation than a traditional control activated sludge process processing the same feed effluent. Due to the bio-inhibitory nature of the feed effluent, the conventional activated sludge failed due to biomass wash out twice during the 100 days of the investigation, while the membrane bioreactor provided a consistent 90% COD removal rate over the entire duration of the test. Due to the increased level of active biomass in the membrane bioreactor, approximately twice the organic loading of the traditional activated sludge process could be achieved (28 vs 15kg$COD_{removed}/m^3$.d) thus allowing a proportionately smaller tank size to be utilised. Male and Pretoruis also report that the oxygen transfer rate in the pressurised reactor was 16 – 35 times that experienced in the traditional, ambient pressure system. Any saving from reduced air requirement may however be offset by the energy costs of pressurising both the air and feed streams to the elevated pressure. The significant increase in capital and maintenance cost of the compressor required to provide this pressure would also need to be taken into account.

A more recent advance in membrane filtration comes with the augmentation of the aeration vessel with an adsorption media such as zeolite or activated carbon. The use of an attached biological culture to regenerate activated carbon beds *in situ* has been investigated for some time now (Miserenz *et al.* 1999) but the use of such media in suspended growth activated sludge systems is now also gaining significant attention. In particular the use of micro- or ultra-filtration membranes for solids separation in the activated sludge process has allowed the use of small particle size, large specific surface area adsorbents such as powdered activated carbon (PAC). Seo and Ohgaki (Seo *et al.* 2001) studied the ultimate fate of bio-refractory compounds treated in the biological PAC – microfiltration system. They found that 82.8% of the organics fed to the reactor were removed by adsorption and subsequent biological oxidation on the PAC. Over 213 days of continuous operation with no external activated carbon regeneration, there was no accumulation of total organic carbon in the system. The synthetic feed stock used in this investigation contained tannic acid, lignin sulfonate, humic acid and arabic gum, which were found to be gradually degraded by contact with the micro-organisms over a period of 20 – 27 days. The benefit of using PAC in such a reactor is that as the organic pollutants are adsorbed onto the carbon, and thus retained by

means of sludge recycle. The actual hydraulic residence time of the reactor can therefore be small (e.g. 12 – 50 hours) while still allowing a high contact time (20+ days) between the organic compounds and active micro-organisms.

Okada *et al* (Okada *et al.* 2000) isolated the influence of attached growth culture on the improvements made in the biological PAC process. In processes where the biological culture was allowed to come in contact with (and subsequently grow on) the activated carbon, approximately 160% more biological growth (and subsequent substrate uptake) was observed than when the same experiment was carried out with the activated carbon separated from the suspended biomass by dialysis tubing. An increase in cell growth of up to 330% was observed by the cells attached to activated carbon, compared to a control culture attached to a non-adsorptive support media (bentonite clay) under otherwise identical conditions.

Other investigations by Lee *et al* (Lee *et al.* 2001) verified that the addition of alum and zeolite to a membrane bioreactor reduced fouling of the membrane due to increased floc size and floc density. Augmentation of the membrane bioreactor with zeolite, which has a high ion exchange affinity for ammonium ions, gave a significant increase in nitrification - denitrification occurring in the reactor. Alum addition gave an increase in biological phosphorus removal from 10% in the control to 90% removal in the reactor containing alum by increased coagulation and settling of poly-P stabilising bacteria. Accumulation of aluminium in the reactor however significantly inhibited nitrification – denitrification.

Trial of a Wehrle Werk cross flow Membrane Bioreactor at a second wool scour in England provided positive results for degradation of organophosphate and synthetic parathyroid pesticide residues. In this case Stork cross flow ultra-filtration membranes were used with a theoretical molecular weight cut-off point of 10,000g/mol. Although ultrafiltration membranes are not of fine enough pore size that the actual pesticide molecules are retained in the reactor by filtration, the pesticides are highly partitioned in dispersed wool grease droplets which *are* retained by the ultrafiltration membrane. This retention of wool grease and subsequently pesticides elevates the concentration of each contaminant in the biological reactor which in turn increases their rate of degradation by the microbial culture. Unpublished results of these trials showed a consistent 85 – 95% reduction in effluent COD to a residual level below 3,500 with a residence time of 30 – 40 hours by this process.

2.2 EVAPORATION

Despite the high capital costs often involved, evaporation as a means of treatment for heavily polluted effluents is becoming common in industry (e.g. wool scours, rendering plants and sugar refineries). This has primarily been due to advances in energy recovery and evaporator design that have enabled minimisation of the overall energy requirement of evaporation to a point where this highly effective technology also becomes economically competitive.

In order to maximise efficiency, most evaporators used for the treatment of wool scouring effluent are multi-stage systems with the evaporated vapour being used as the heating medium. This requires some form of mechanical or thermal compression of the evaporated vapour to a higher temperature in order to provide a driving force for heat transfer to the feed liquor.

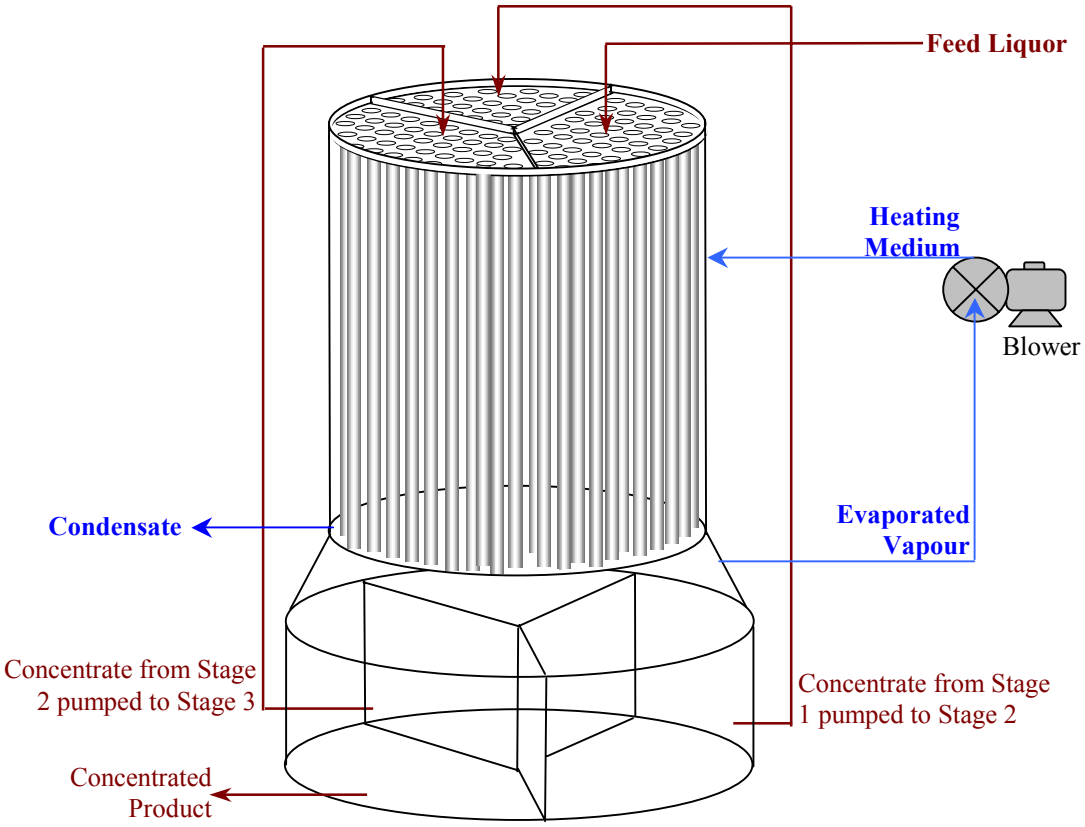


Figure 2.8 The principal of mechanical vapour recompression, falling film evaporation

The most successful application of this technology to wool scouring effluent treatment has been the Evatex Mechanical Vapour Recompression (MVR) falling film evaporator design, which uses multiple liquid stages inside one common vapour shell (similar to Figure 2.8). In

this case the liquor passes sequentially through a number of stages of tube bundles, becoming increasingly concentrated from stage to stage. The vapour evaporated from each stage is combined, compressed to a higher pressure (and therefore temperature) by use of a large centrifugal blower, and passed into the common shell side of the falling film evaporator where it condenses on the outside of all of the tube bundles providing the heat required for evaporation. This condensate is then removed via a further heat recovery system as the final product of the evaporator. As water is driven off by evaporation the viscosity of the concentrated liquor increases until no further concentration can be carried out by falling film evaporation. Thus, to achieve final concentration of the effluent in the Evatex system, two forced circulation evaporation stages are used. In the forced circulation stages, concentrated effluent is pumped through tube bundles in separate shell side vessels. Due to boiling point elevation of the concentrated liquor, the heating medium for this operation must be further compressed from the shell side of the falling film evaporator. To achieve this, high-pressure process steam is usually added.

Figure 2.9 Falling film MVR evaporation plant for treatment of wool scouring effluent

The result of this system, a full scale application of which is pictured in Figure 2.9, is a very clean condensate phase (COD < 100mg/L) and a concentrate which varies from a potassium and sulphur rich liquid, to a high dirt content sludge depending on what pre-treatment processes are used prior to evaporation. Although this condensate is of low COD, the carry over of volatile compounds such as ammonia and low boiling point organics means that further treatments such as reverse osmosis or ozonation are often required for residual colour and odour removal if the condensate is to be recycled back to the scouring line as wash water.

2.3 FUTURE DIRECTION OF EFFLUENT TREATMENT TECHNOLOGY IN INDUSTRY

One of the key results of increasing international awareness of environmental issues is the widespread implementation of stringent effluent discharge limits and costly discharge fees imposed on industry based on the strength of the effluent that they discharge from site. These regulatory constraints are in turn providing the economical incentive required for industry to invest in on-site effluent treatment systems.

As the sustainability of industrial processes comes under ever increasing scrutiny, this requirement for on-site effluent treatment is set to take a more important role than ever in the operations of many industrial sectors. One result of this is an increase in the development of new effluent treatment processes such as the advanced biological and physical systems described in this chapter.

As the technology becomes more established, and the cost of materials continues to decline, the implementation of membrane-based bioreactors is set to replace traditional activated sludge plants in applications where specialised substrate removal or space constraints are the dictating factors. This technology is also in a position to significantly extend the capacity of existing activated sludge processes by replacing the secondary clarifier with membranes to boost the operating MLSS and subsequent product quality.

Similarly, in cases where extremely stringent discharge consents are imposed (such as in much of Europe), the implementation of technology that has previously been economically infeasible is becoming more and more common. In particular, the ability of evaporators to produce a product that can either be discharged to surface waters, or recycled for re-use as process water is making these otherwise expensive pieces of equipment not only feasible, but an attractive option in many industry sectors such as wool scouring.

3 ANALYTICAL PROCEDURES

3.1 SUSPENDED SOLIDS

3.1.1 DESCRIPTION

Suspended Solids testing was carried out extensively on site and in the laboratory and occasionally by accredited laboratories (IANZ accredited or similar) in accordance with APHA 20th Edition 2540D. (Clesceri *et al.* 1998). In the biological systems investigated, Mixed Liquor Suspended Solids (MLSS), as tested by this method, was used as a measure of the quantity of biomass present in the biological system. This parameter was considered acceptable, rather than using the more rigorous (and time consuming) volatile suspended solids test, due to the fact that almost all of the non-volatile solids have been removed by the Sirolan CF process prior to any biological treatment. A summary of the method used is given below.

3.1.2 EQUIPMENT USED

Glass Fibre Filter Discs Without Organic Binder

Whatman grade 934AH, filter discs (or similar) were used for all tests carried out in the laboratory or on site. The diameter of the filter discs was selected to fit closely inside the vacuum filter funnels available.

Membrane Filter Funnel

This was a funnel with a perforated disc fitted as a filter support. The funnels used were of ceramic construction with rubber flask stoppers for attachment to a suction flask.

Suction Flask

This was a conical flask of approximately 250mL volume with a top that could be sealed to the filter funnel and a hose attachment in the neck of the flask for connection of a suction line as illustrated in Figure 3.1.

Suction Pump

This was a venturi pump that when connected to a mains pressure water supply provided a suction of air into the venturi.

Drying Oven

A range of ovens were used that could be operated stably at 103 – 105°C as required.

3.1.3 PROCEDURE

1) The apparatus was set up as shown in Figure 3.1, using a rubber hose to connect the suction pump to the suction flask as depicted.

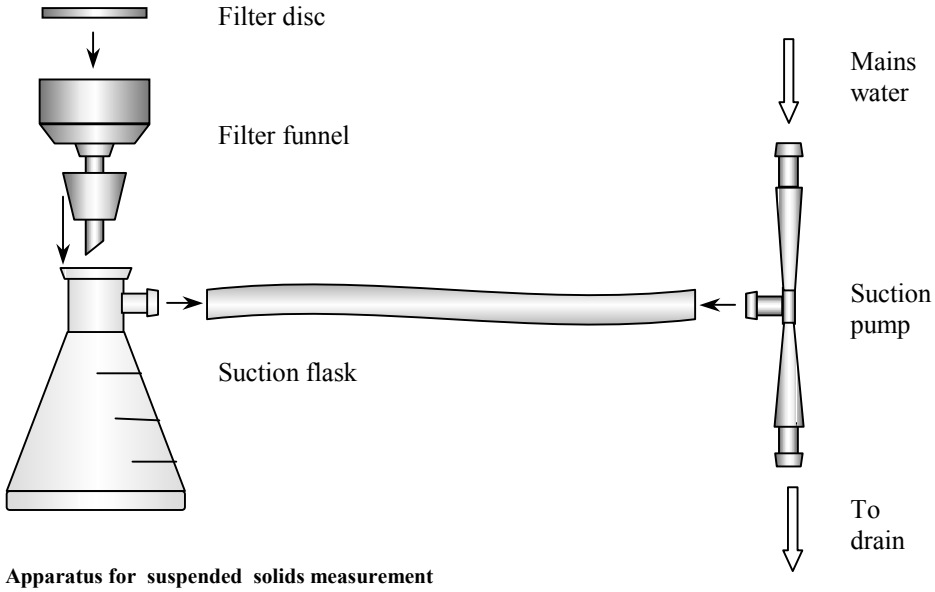


Figure 3.1 Apparatus for suspended solids measurement

2) With the filter disc in place (wrinkled side up), suction was applied. Approximately 60mL of distilled water was passed through the filter in order to wash it. Suction was then left on for at least three minutes after washing to remove all traces of water. All water collected in the flask at this stage was discarded.
3) The filter was dried to a constant weight in a desiccator.
4) The filter disc was weighed.
5) The filter disc was returned to the filter apparatus and suction applied. A small volume of water was applied to seal the filter disc to the perforated support plate of the filter funnel.
6) While stirring the sample to be tested, a known volume of sample was pipetted onto the filter disc using an Eppendorf 1,000 – 5,000µl research pipette.
7) The sample was then washed by pipetting three successive 10mL volumes of distilled water through the filtered sample on the disc. Suction was continued for three minutes after filtration and washing were complete.

8) After suction was stopped, the filter disc was carefully transferred to an aluminium weighing tray. The tray and disc were inserted in the drying oven at 103 – 105°C for at least one hour. The dried sample was then allowed to cool to ambient temperature in a desiccator and weighed. Finally the liquid collected in the flask was discarded.

3.1.4 CALCULATION

$$\text{Total suspended solids [mg/L]} = \frac{(A - B) \times 1{,}000}{\text{sample volume [mL]}}$$

Where:

A = Weight of filter + dried residue [mg]

B = Weight of filter [mg]

3.1.5 NOTE ON ACCURACY

- Samples were mixed to ensure complete solids suspension prior to and during sample taking. In none of the analysis carried out by the author were the samples homogenised by use of a food processor, ultrasonic probe, or any other high intensity mixing system prior to analysis. Stirring was generally carried out by magnetic rod mixer. Due to the large sample sizes used for analysis the lack of homogenisation is not believed to have introduced any significant errors.
- As long as the filter is not overloaded, the greater the sample volume used, the more accurate the suspended solids test will tend to be. In the analysis carried out, the volume of sample passed through the filter was chosen to provide a target level of > 0.1g of dried suspended solids on the filter medium.
- The Mettler Toledo mass balance used to determine mass of dried solids had a minimum resolution of 0.0001g, so if the level of > 0.1g of dried solids were achieved, there would be less than ±0.2% error in the weight measurement.
- The 1 – 5mL Eppendorf Pipette used had a repeatability of ±0.010ml, which is ±0.02% of the typically 10mL samples.

3.2 TOTAL SOLIDS

3.2.1 DESCRIPTION

Total Solids measurements were primarily carried out by NZIA accredited Laboratories in accordance with APHA 20th Edition 2540B (Clesceri *et al.* 1998). Those carried out on site followed the format summarised below:

3.2.2 APPARATUS USED

Evaporating dishes

Approximately 100ml capacity made of stainless steel, aluminium, or ceramic material.

Drying Oven

An oven operating in the temperature range 103 – 105°C was used.

Desiccator

This was a sealable vessel containing a quantity of calcium sulphate or silica gel to adsorb any water vapour present. In the laboratory a commercially produced desiccator with indicating desiccant was used, whereas for field analysis at wool scours a sealed container containing silica gel was used.

3.2.3 PROCEDURE

1) A sample representative of the overall mass of liquid or sludge to be tested was taken.
2) The evaporating dish was weighed.
3) A known volume of liquid was transferred from the well mixed sample to the dish.
4) The sample was placed in the drying oven until no visible liquid remained, then left in the oven for one more hour to complete drying.
5) The evaporating dish and sample were removed from the oven and cooled to ambient temperature in the desiccator unit.
6) The evaporating dish with the dried sample was weighed.

3.2.4 CALCULATION

$$\text{Total solids [mg/L]} = \frac{(A - B) \times 1{,}000}{\text{sample volume [mL]}}$$

Where:

A = Weight of dried residue + dish [mg]

B = Weight of dish [mg]

3.2.5 NOTE ON ACCURACY

If the desiccant used was expended, or a desiccator not used, then the dried sample in both the total and suspended solids test would adsorb sufficient atmospheric moisture during cooling to invalidate the result. This proved particularly relevant in the humid environment found in most wool scours. Great care should therefore be taken to follow procedure closely in such environments.

3.3 BOD_5 (BIOLOGICAL OXYGEN DEMAND FIVE DAY TEST)

This test measures the amount of oxygen taken up by an acclimatised microbial culture when exposed to the water sample for a five-day period. It is primarily used to determine the level of oxygen depletion that will occur if the effluent stream tested is discharged to a natural waterway or biological treatment plant, and is a common parameter used by regulatory authorities to monitor and control industrial effluent quality.

Due to the high set up cost and labour intensity of the analysis method, BOD_5 testing was carried out entirely by IANZ accredited laboratories in accordance with APHA 20th Edition 5210B (Clesceri *et al.* 1998)

3.4 COD (CHEMICAL OXYGEN DEMAND)

3.4.1 DESCRIPTION

Chemical Oxygen Demand is a measure of the total quantity of oxidisable compounds present in a liquid solution. Potassium dichromate in a concentrated sulphuric acid solution is used to oxidise the sample and the reduction of potassium dichromate is then measured by colorimetery.

Due to the speed, low setup cost and ease of use, it was considered practical to purchase test equipment for this analysis for the use of this project. This testing was carried out using the closed reflux colorimetric method both in IANZ accredited laboratories and on site in accordance with APHA 20th Edition 5220D (Clesceri *et al.* 1998).

3.4.2 APPARATUS USED

1mL Pipette

An Eppendorf micropipette of 100 – 1000μL capacity was used for measuring liquid samples.

COD reagent vials.

These are sealable test tube sized vials containing the potassium dichromate / sulphuric acid / mercuric sulphate solution required for the oxidation process. This reagent could be made up in the laboratory in accordance with APHA 20th Edition 5220D (Clesceri *et al.* 1998) but for increased accuracy and safety pre-prepared reagent vials were purchased.

For COD ranges 1,000 – 1,500 Hach HR COD reagent vials were used.
For COD ranges 1,500 – 15,000 or above Hach HR+ COD reagent vials were used.

Some analysis was carried out using laboratory prepared reagent vials but, due to lack of repeatability, these results were discarded and all results reported herein were obtained using the Hach HR+ commercially prepared reagent vials.

NOTE: Whether commercially supplied or laboratory prepared reagent vials are used, great care must be taken in handling vials (especially when adding samples) as the liquid reagent is highly toxic and corrosive. As minimum protection, safety glasses and protective gloves were worn whenever handling the reagent.

COD Reactor

This was a heating block that could be operated at 150°C ±1°C with holes sized to accommodate the COD reagent vials chosen. The reactor had a two-hour timer integrated into the power supply system so that the heater cut out after digestion was complete. The model used was the Hach COD Reactor.

Colorimeter

A colorimeter / spectrophotometer capable of measuring absorbance at 600nm was used. The colorimeter used was a Hach DR/890 portable colorimeter. On this unit the absorbance result presented by the meter was a direct value for COD generated by an internal conversion. By using a Hach colorimeter there was also no need to transfer the digested reagent into a spectrophotometer vial as the measurement cell is sized for direct insertion of the reagent vials, thus improving safety and reliability of the process.

3.4.3 PROCEDURE

1) A representative sample of the bulk liquid to be tested was taken.
2a) If the sample was expected to have COD < 15,000mg/L (i.e. Rinse Water, CFB centrate, or good CF centrate), 0.2mL of sample was then pipetted directly to a Hach HR+ reagent vial.
2b) If the sample was expected to have COD in the range: 15,000 < COD < 30,000mg/L (most Sirolan CF centrate) then the sample was diluted by a factor of one by adding 500mL of distilled water to 500mL of sample in a 1L measuring cylinder before pipetting 0.2mL of the mixed diluted sample into a Hach HR+ reagent vial.
2c) If the COD was expected to fall in the range 30,000 < COD < 150,000mg/L (i.e. most heavy flow-down liquor) then the sample was diluted by a factor of 10 by adding 100mL of sample to a 1L measuring cylinder and making the total volume up to exactly 1000mL by adding distilled water. 0.2mL of this mixed diluted sample was then pipetted into a Hach HR+ reagent vial.
3) To a separate reagent vial 0.2mL of distilled water was added (the same water used for the dilutions). This acted as the blank reference for zeroing the colorimeter. One blank sample was prepared for each set of samples simultaneously digested.
4) The reagent vial was then placed in the COD reactor (Heating Block) for two hours at 150°C ±1°C.

If the reactor was in close proximity to other workers then a protective screen was used to protect them against the eventuality of reagent vial rupture and subsequent splashing of high temperature corrosive chemicals.

5) The vials were allowed to cool (either in reactor or in a test tube rack).
6) When cool, the blank sample was inserted into the colorimeter and the 'zero' key on the colorimeter pressed.
7) Finally, the test sample vial was inserted in the colorimeter, the appropriate preset program for the vials used was selected (Hach HR+, or as per colorimeter operating instructions), and COD result read directly off the colorimeter's LCD screen.

3.4.4 CALCULATION

The following applies to the use of Hach HR+ pre-mixed COD reagent vials. If using a different COD digestion reagent refer to the supplier instructions for calculation method.

- If the COD of the original sample was expected to fall between 0 < COD < 15,000 (as in option 2a above) then the COD of the original sample was the COD displayed by the colorimeter multiplied by ten.

- If the COD of the original sample was expected to fall between 15,000 < COD < 30,000 and was prepared as per option 2b above, then the COD of the original sample was exactly twenty times that displayed by the colorimeter.

- If the COD of the original sample was expected to fall between 30,000 < COD < 150,000 and was prepared as per option 2c above, then the COD of the original sample was exactly one hundred times that displayed by the colorimeter.

3.5 PH

In all cases pH was measured with a glass bulb pH meter, connected to a digital display. pH probes were calibrated with pH 7 and pH 4 buffer solutions once every two to four weeks. pH results reported for Sirolan CF or bioreactor operation were all measured by in-line or in-tank pH probes continuously monitoring the effluent stream.

3.6 DISSOLVED OXYGEN (DO)

3.6.1 DESCRIPTION

Dissolved oxygen was measured by a probe consisting of a platinum cathode and lead anode immersed in potassium chloride electrolyte, and separated from the test sample by a PTFE membrane. Probes were calibrated using oxygen depleted and oxygen saturated samples of the liquid to be tested.

3.6.2 PROBE CALIBRATION

Oxygen free standards (zero reference) were generated using the following procedure:

i. Take a 250mL sample of the liquid to be tested and sparge with nitrogen for 30 minutes.

   Or:

ii. Add to a 250mL sample of the liquid to be tested:
   - 10g of Sodium Sulphate
   - 0.1g of Cobalt Chloride

   Stir gently for 1 minute

Oxygen-saturated standards (100% span on DO probe) were generated by sparging air through a 250mL sample for at least 30min.

NOTE: If the sample to be used for oxygen saturation standard contained biological growth (i.e. Sirolan CF-B liquor) then samples were acidified to pH3 with sulphuric or nitric acid before aerating. Sparging was only stopped immediately prior to using the calibration solution.

To calibrate the probe:

1) The probe was inserted in the oxygen-depleted sample while gently stirring the sample.
2) Once a stable reading was achieved the calibration of the meter connected to the probe was set to 0%.
3) The probe was inserted in the oxygen saturated sample.
4) Once the meter reading had stabilised the meter calibration was set to 100%.

3.7 SOLVENT EXTRACTABLE FRACTION (WOOL GREASE + DETERGENT)

Wool grease analysis was carried out by IANZ accredited laboratories using the Soxhlet Extraction Method in accordance with APHA 20th Edition 5520D (Clesceri *et al.* 1998).

3.8 MISCELLANEOUS ANALYSIS

Nitrate, Nitrite, Ammonia Nitrogen, Total Nitrogen (TKN), Dissolved Reactive Phosphorus, and Phenols analysis were all carried out by IANZ accredited Laboratories in accordance with APHA Standard Methods 20th Edition (Clesceri *et al.* 1998).

4 EXISTING WOOL SCOUR EFFLUENT TREATMENT SYSTEMS

During the course of this research, a total of five months were spent on site at various wool scours throughout the world working with their effluent treatment plants and evaluating the potential for integration of the technology described in this thesis. The following case studies detail the effluent treatment processes used at four of these sites. Due to the commercial sensitivity of the information presented, measures have been taken to prevent the identification of the individual wool scours in question. None of the omissions made affect either the relevance or accuracy of the information presented.

4.1 CASE STUDY 1

4.1.1 OVERVIEW

Local Discharge Consent:	Zero Liquid Discharge from site
Typical Actual Discharge:	Occasional discharge of 'off spec water' to drain under temporary permit
Approximate Capital Expenditure on Effluent Treatment:	NZ$ 17 – 20 Million (1999)
Technologies Used:	3 Stage Wool Grease Recovery Solids Recovery by Hydrocyclones and Decanter MVR Evaporation Air Stripping Steam Stripping Reverse Osmosis

4.1.2 PROCESS DESCRIPTION

Case study 1 is a large, multiple scouring line plant primarily processing low yield merino wool. In this plant, due to the fine diameter of the wool being processed and the high level of contaminants deeply entrained within the fleece, a smaller than normal fraction of the dirt and

grease entrained in the fleece is removed by the wash bowls. As a result of this, more of these contaminants are still present in the wool when it enters the rinse bowls and the waste rinse water is accordingly more heavily contaminated by these fractions than is generally found elsewhere.

In strong contrast to established practice, in this plant the still relatively clean rinse water and heavily polluted wash water from the two sections of the scour are combined before being passed on to the effluent treatment plant.

Prior to combining the waste streams, the heavy flow-down component is passed through a three-stage wool grease recovery plant. The wool grease recovery plant is an integrated part of the scouring plant, while the effluent treatment plant is a separate entity located some distance from the wool processing building.

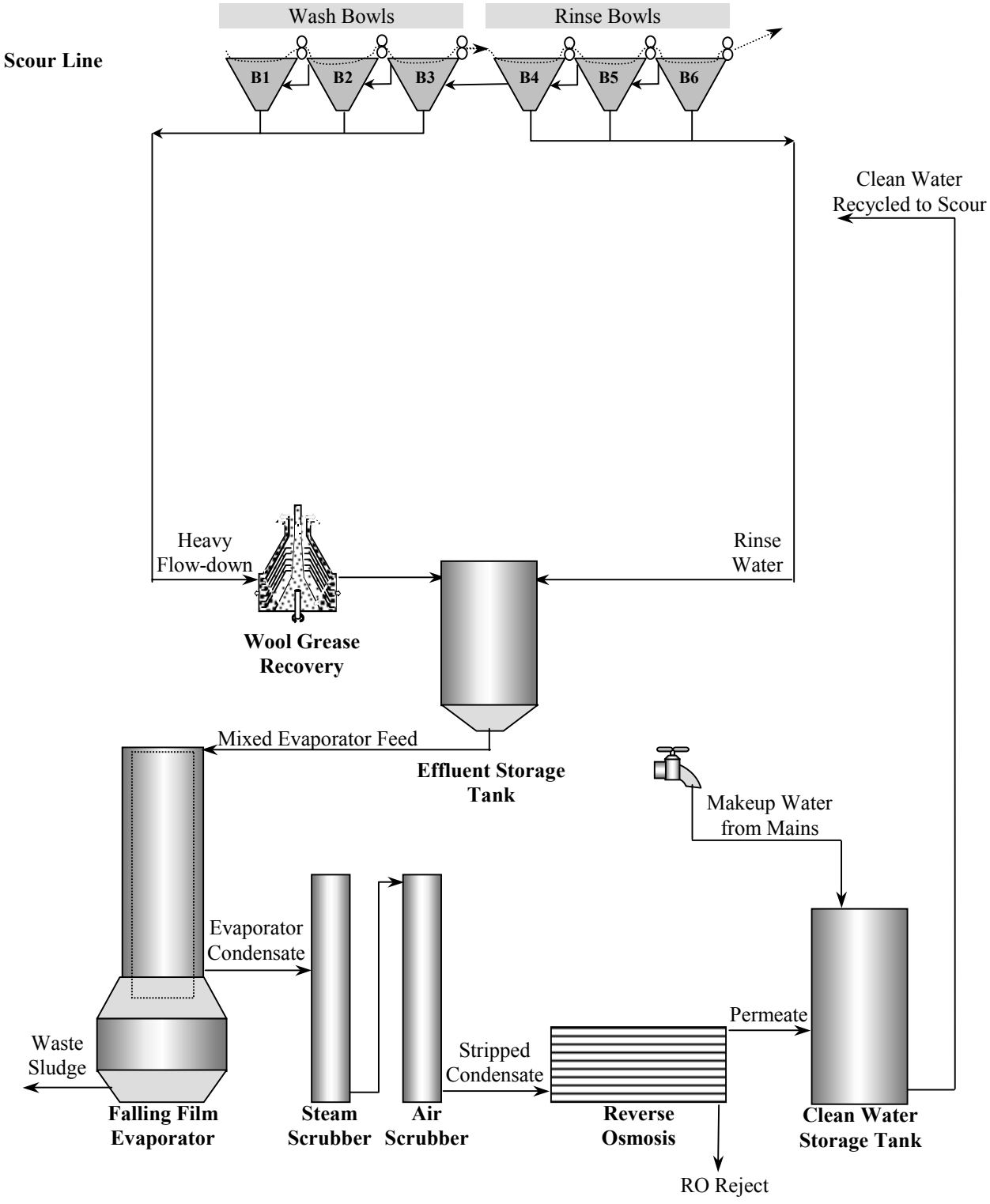


Figure 4.1 Case study 1, scouring lines and effluent treatment plant

Table 4.1 Effluent characteristic summary for case study 1 (Refer Figure 4.1)

	Mixed Evaporator Feed	Evaporator Condensate	Stripped Condensate	RO Permeate
SS $_{mg/L}$	6,200	27	88	< 1
COD $_{mg/L}$	17,000	1,200	580	65
Wool Wax $_{ppm}$	755	30	39	17
Phenols $_{ppm}$	434	76	60	18

Note: Values presented are spot values recorded during a visit to site by the author

The evaporator used is a multiple effect, falling film, mechanical vapour recompression design with a small forced circulation finishing stage for the concentrated sludge produced by the falling film effects (which is unsuitable for further treatment in a falling film due to it's elevated viscosity). The evaporator has been sized such that sufficient heat exchange surface is available to allow a mean temperature difference as low as 5°C to be used to drive the heat transfer. As an increase in temperature of 5°C can be achieved by compressing the evaporated steam by only 20kPa (Rogers *et al.* 1995), a centrifugal fan can be used to compress the evaporated steam to the point where it can be used as the heating media. The advantages that this has over reciprocating (or similar) compressors usually required for mechanical vapour recompression are the greatly reduced capital, operating and maintenance costs of a centrifugal fan system.

As can be seen from Figure 4.1, there is no facilitation of solids removal from the effluent prior to evaporation. This means that the liquor being fed to the evaporators contains as much as 7,000mg/l suspended solids. This has led to two main problems in the operation of the process:

1. Periodic accumulation and subsequent release of slugs of heavy solids in the hopper-bottomed effluent storage tank prior to the evaporator (Figure 4.1) has introduced instability into the flow through the entire effluent treatment plant.

2. The sludge removal from the base of the falling film evaporator is by gravity flow along the floor of the vessel, which is inclined at no more than 10° to the horizontal. This system was not designed to accommodate the extreme loading of heavy solids being passed through the evaporator and regularly requires full plant shutdown to manually remove the subsequent solids build-up with shovels and buckets.

In the course of this study, four weeks were spent on site at this wool scour carrying out an evaluation of the effluent treatment plant and developing solutions to operational problems that have been encountered since commissioning. In this time, one shift was spent inside the calandria at the base of the evaporator assisting with the removal of 4 tonnes of heavy solids and sand that had accumulated over the preceding month. To allow the evaporator to cool to a temperature where it is possible to work inside it, the entire scour must be shut down for 30 – 36 hours. A further 10 - 12 hours are required to remove the solids build-up and restart the effluent treatment plant.

After evaporation, the effluent is steam stripped and air stripped in two large gas contacting columns of bubble cap and packed bed design respectively. These processes remove a large fraction of the residual volatile organic contaminants that contribute to the odour and residual COD of the condensate at this stage.

The final stage of the process is to pass the stripped condensate through a reverse osmosis plant where almost all of the ionic compounds still present are removed. Many problems have been experienced with the throughput of the reverse osmosis plant, which had to be doubled in size soon after commissioning due to disproportionate flux drop off. Much trouble has also been encountered with permanent poisoning of the RO membranes which have so far required replacement at an expense of over NZ$700,000 per six months. The scour owners are currently working in co-operation with the membrane manufacturers to overcome this problem. The permanent poisoning of the RO membranes has been primarily attributed to compaction of the membrane support base, which has been softened by unexpected concentrations of cresols and phenols in the RO feed. (Macintosh 1999). This accumulation of phenols in the recycle loop between the effluent treatment plant and the scouring lines has been verified by a number of independent sources (Macintosh 1999) but their source remains unclear. The detergents used in wool scouring are nonylphenol ethoxylate based, but studies by membrane producers (Macintosh 1999) showed no raw phenol or cresol (4-Ethyl Phenol) compounds present in the detergent, and were unable to produce any by steam stripping or chemical reaction of the detergent with the other compounds found in the liquor. Mammal urine in general contains traces of the dominant cresol (para-methyl phenol)detected in the accumulation loop (World Health Organisation 1996), but without a measure of the level of this compound on unwashed sheep fleece or a degradation mechanism for nonylphenol ethoxylate detergent to these derivative phenol fractions the source of the phenol accumulation remains inconclusive.

As the source of the phenolic compounds could not be identified the following method of removal was proposed:

The Alkyl Phenol derivatives in question are significantly more volatile in their non-ionic 'acid' form, which occurs below a pH of approximately 9.3, (Macintosh 1999). The effluent sent to the steam and air strippers for volatile organic removal is typically pH 9.6 – 9.8, so neutralisation of this liquor to pH 8.5 or lower could significantly improve the removal of phenolic compounds while costing less than NZ$4,500pa at an average effluent flow rate of $20m^3/hr$ (Savage 2000).

Although the wool scour in case study 1 operates under a 'zero discharge' resource consent, they have regularly had to operate under a temporary discharge consent to allow a small purge stream to the local sewer. This is due to a number of factors including insufficient capacity for reprocessing off-spec effluent and the need for a purge stream in the recycle loop to prevent excessive accumulation of organic compounds.

4.2 CASE STUDY 2

4.2.1 OVERVIEW

Local Discharge Consent:	COD to River < 100mg/L SS to River < 50mg/L
Approximate Capital Expenditure on Effluent Treatment:	~ $NZ 50 million (1990)
Technologies Used:	Gravity Separation of Heavy Solids Centrifugal Removal of Heavy Solids 2 Stage Wool Grease Recovery Evaporation Incineration Low Rate Aerobic Biological Treatment

4.2.2 PROCESS DESCRIPTION

Case study 2 details possibly the most comprehensive wool scour effluent treatment plant in the world. Due to the wide publication of the details of this process in open literature (Hoffmann *et al.* 1996a; Hoffmann *et al.* 1996b), this installation can be named. Bremer Woll-Kämmerei AG (hereafter BWK) is located on the shores of the river Weser near Bremen in Northern Germany where it operates a plant consisting of eight parallel wool-scouring lines. The effluent from these scouring lines is treated by a comprehensive combination of wool grease recovery, anaerobic biochemical flocculation, aerobic activated sludge treatment and evaporation-incineration. The layout of the plant, as adapted from Hoffmann (Hoffmann *et al.* 1996a) is depicted in Figure 4.2.

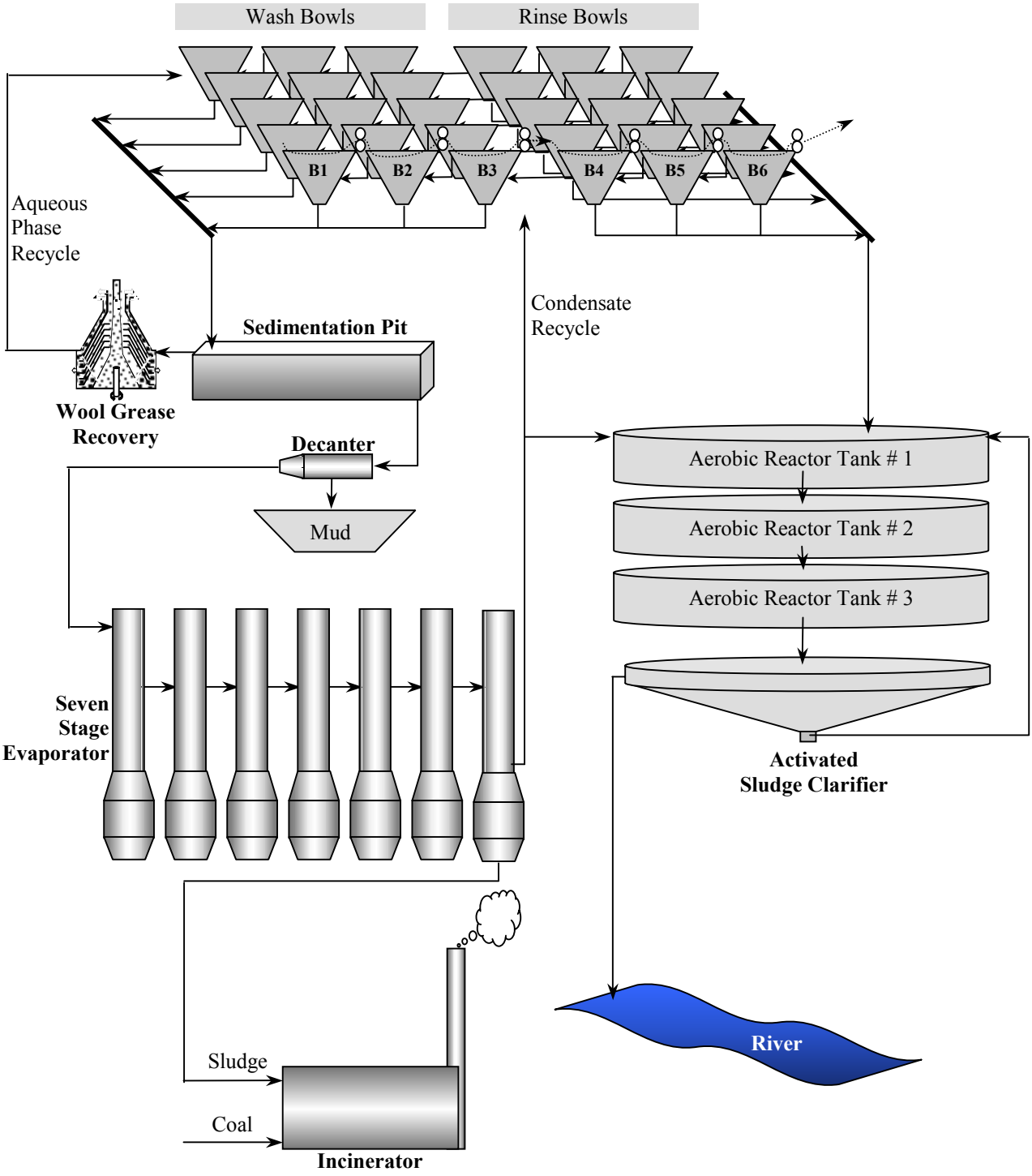


Figure 4.2 Case study 2, scour lines and effluent treatment plant.

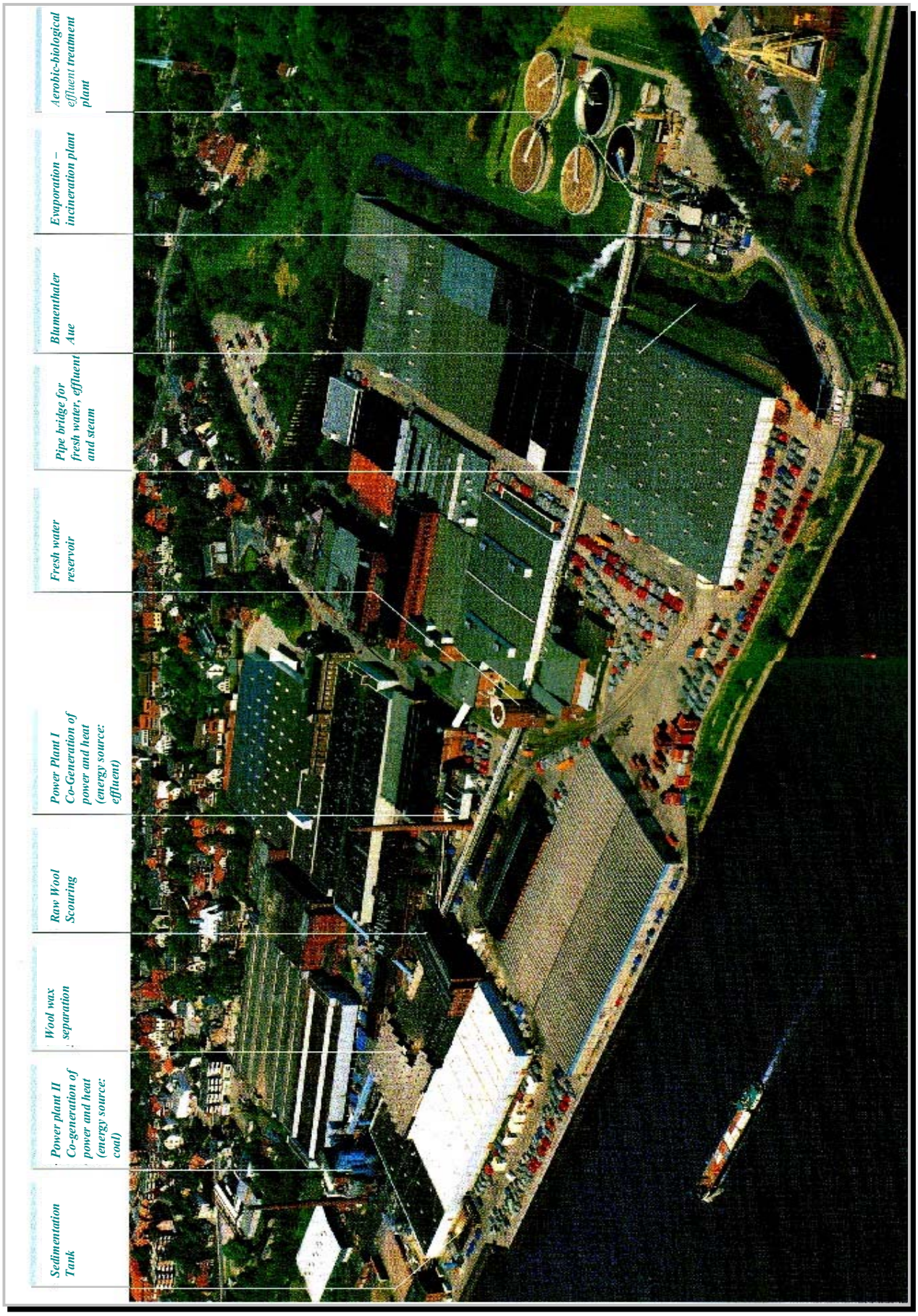


Figure 4.3 Aerial view of BWK Bremen plant showing scouring and effluent treatment plant locations. (Hoffmann *et al.* 1996a)

Key features of this plant are:

Sedimentation Pit

The sedimentation pit was primarily built with sand separation in mind. The goal was to remove heavy abrasive solids from the feed to the wool grease recovery plant while thickening those solids in preparation for feeding to a solids removal decanter.

The sedimentation pit actually consists of two flat bottomed rectangular basins, each of 2500m^3 capacity. Both of these pits are fitted with a mechanical sludge scraper, which is used to rake sludge along the base of the pit to the solids discharge auger at one end. This scraper arrangement is shown suspended in an empty pit in Figure 4.4.

Figure 4.4 Empty sedimentation pit basin showing sludge scraper

Figure 4.5 Floating draw-off shown in empty BWK settling pit

Both of the sedimentation basins are also fitted with a floating surface draw-off, from which a grease rich phase in the top of the pit is taken to the wool grease recovery plant. Figure 4.5 shows the floating grease draw-off assembly suspended in an empty sedimentation basin. As the liquid level in the basin rises, the floats on either end of the assembly ensure that the draw-off point is always at the liquid surface, thus maximising the quantity of grease recovered.

These basins are of sufficient size to give five days hydraulic retention time of the entire heavy flow-down effluent from all eight scouring lines. With such extended residence time in the settling pit, significant anaerobic growth is established in the effluent prior to passing to wool grease recovery or further treatment. The actual flow path of the effluent to and from the pits is detailed in Figure 4.6.

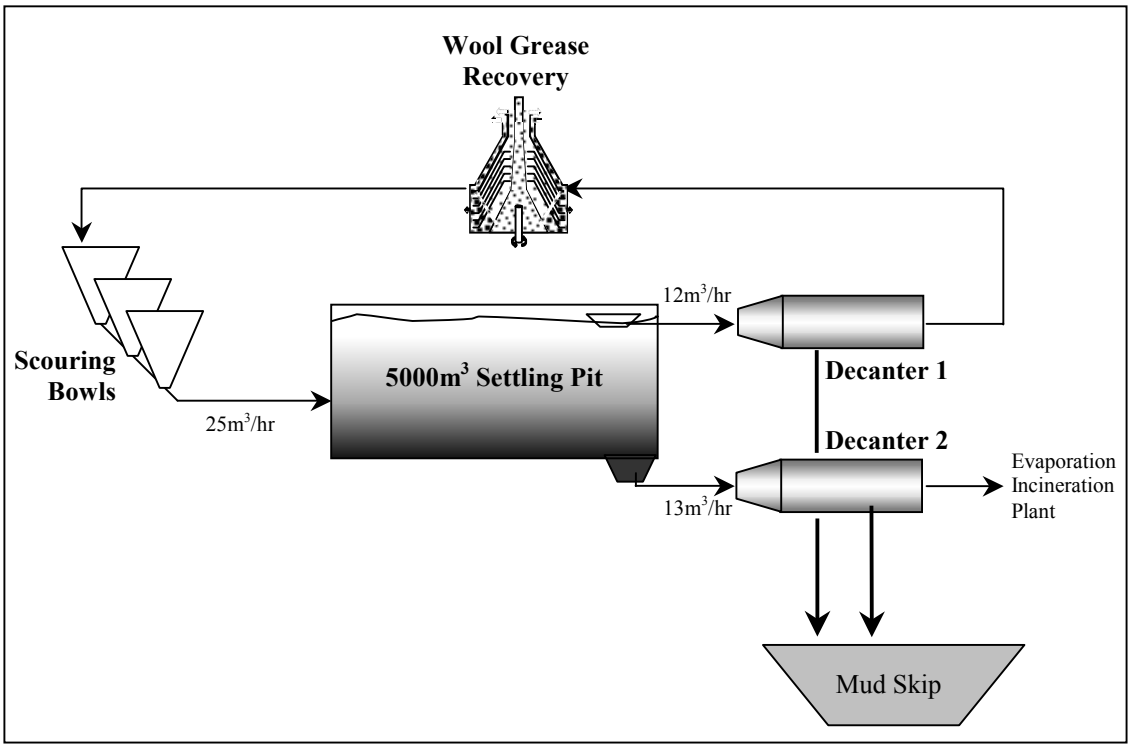


Figure 4.6 BWK settling pit flow diagram

The grease rich phase in the top of the settling pit is drawn off after five days and any heavy solids removed in decanter 1 before the effluent is sent on to the wool grease recovery plant. This sequence of separation processes along with the anaerobic bio-flocculation and detergent breakdown occurring in the settling pit (See Section 5.2 for detail of the processes involved here) result not only in a very efficient recovery of wool grease, but also in improved quality of this wool grease due to the low level of residual detergent in the final product.

The heavy phase from the settling pit is passed through decanter 2, from which a large portion of the solids are collected. This process is also aided by the anaerobic floc formation and pre-thickening that occurs in the sedimentation pit. This process produces both a very dry sludge and a decanter centrate with low residual solids. The high quality centrate from Decanter 2 is then fed to the evaporation incineration plant.

The one disadvantage of the current operation of this heavy solids and grease recovery loop is that the anaerobic liquor from the settling pit, after having passed through the wool grease plant, is returned to the washbowls as wash water. Here the anaerobic liquor is black in colour and carries a strong 'anaerobic smell' of hydrogen sulphide, which can be adsorbed into the wool, potentially compromising the ultimate product quality.

Evaporation - Incineration

At BWK the key form of heavy effluent treatment is by evaporation combined with incineration, which burns the high-energy residue of the evaporation process. The evaporation is carried out under vacuum in seven separate falling film stages. The heating medium is passed from stage to stage, counter current to the effluent flow. Evaporated steam from each stage is combined with process steam on the shell side of the evaporators and passed on as heating media for the next stage, where it condenses on the outside of the falling film tubes and is collected. Due to the efficiency of the evaporation process and the high energy content of the concentrated effluent (approx. 9,500kJ/kg -(Hoffmann *et al.* 1996a)) the subsequent process steam requirement of the evaporator is actually less than that which can be produced by burning the concentrate from the process. The plant is therefore equipped with a cogeneration turbine that is used to generate electricity from the excess steam produced.

Figure 4.7 BWK evaporation – incineration plant (Hoffmann *et al.* 1996a)

The cogeneration of steam and electricity from incineration of wool scouring waste is seen as a great advantage in Germany. Not only does it make the process self-sufficient in energy terms but also, due to local legislation, any electricity generated from a renewable resource (including wool scour waste) can be sold into the national power grid, and the electricity supply company receiving it must by law pay a premium price to the generator.

Condensate Treatment

After the steam produced by evaporating the wool scour effluent is condensed, this condensate is steam stripped to remove ammonia and then passed through a fixed film bioreactor to remove any steam volatile pesticides and residual organic compounds. Approximately two thirds of this processed condensate is then recycled back to the scour as wash water. The remaining condensate is purged from the system and fed through the biological rinse water treatment plant prior to being discharged into the local river.

Great care is taken at this site to maintain the quality of the flue gas discharge from the incineration process. Firstly the incineration process operates as a two-stage combustion system to reduce nitrogen oxide emissions. Stage one operates under low oxygen concentration, which gives low nitrogen oxide production. The second stage is carried out with an excess of oxygen to convert the carbon monoxide generated by the first stage to carbon dioxide. A selective non-catalytic reduction process then uses ammonia (recovered from the scour condensate by steam stripping) fed directly into the flue gas to trigger further nitrogen oxide reduction. In this process the ammonia reacts selectively with the nitrogen oxide present in the gas, producing nitrogen gas and water. These combined processes achieve a final nitrogen oxide concentration in the discharged gas of less than 200mg/m^3.

In order to reduce the particulate emissions from the incineration process, the original wet scrubber used to treat flue gas was augmented with a bag filter. By means of this process, particulates including potash and soda are collected. The water soluble salts are then separated and recycled to the scour bowls where they aid in the scouring process. The bag filter – wet scrubber combination gives a reduction in total particulate emission in the flue gas to 5mg/m^3, which is half the discharge consent limit as per the 17th Federal Emission Protection Ordinance. (17.BlmSchV 1990)

Rinse Water Treatment

Figure 4.8 Biological rinse water treatment basins at BWK (Hoffmann *et al.* 1996a)

The rinse water treatment system employed by BWK is a biological activated sludge system consisting of four 35m diameter, 6m deep aeration basins (Figure 4.8) of which three operate in series (as shown in Figure 4.2) and the fourth is held in reserve. A three-stage sludge settling, thickening and dewatering system is used to separate the activated sludge from the processed effluent and concentrate it into a reusable form. The 10 ton per day of dewatered biological sludge produced is applied to farm land as a nitrogen and potassium rich fertiliser.

As this biological treatment process was constructed prior to the evaporation – incineration plant, it was originally designed to process the scour's entire combined effluent loading, including both rinse water and heavy flow-down. Now that the heavy polluted flow-down from the wash bowls is processed by the evaporation – incineration plant, the biological treatment system would have an available hydraulic residence time in the aerated tanks of approximately sixty days if treating rinse water alone. To better utilise the available waste water treatment capacity provided by these reactors, the rinse water feed to the treatment plant is augmented with other waste streams both from onsite sources, such as textile shrink-proofing, and local industries such as photographic processing laboratories. The quantity of effluent above and beyond the rinse water flow that is currently treated in the activated sludge process is not publicly known.

The product from the activated sludge system is of extremely high quality and is discharged directly to the river Weser. Typical contaminant levels in the effluent discharged to the river are given in Table 4.2:

Table 4.2 BWK discharge contaminant levels (Hoffmann *et al.* 1996a)

COD	120 mg/L
BOD_5	< 5 mg/L
Total Nitrogen	30 mg/L
Phosphate	2 mg/L

4.3 CASE STUDY 3

Local Discharge Consent:	BOD_5:	1,200 kg/day
	Solids:	1,050 kg/day
	Wool Grease:	360 kg/day
Approximate Capital Expenditure on Effluent Treatment:	$NZ 3 million (1999)	
Technologies Used:	3-stage Wool Grease Recovery	
	Evaporation / Incineration	

Case study 3 is a single scour line processing primarily crossbred fleece and slipe wools. This plant is situated in an environment where, although the cost of water supply and discharge of low strength effluent (to river) is very low, the environmental consequences of discharge of stronger effluents to river would be unacceptable. The plant not having access to a municipal wastewater treatment plant further complicates this situation. These constraints have led to the successful combination of using a low flow of liquor in the wash section of the scour and treating it to the extent that it can be completely recycled as wash water, while running a very large quantity of water through the rinse bowls and discharging it directly into a nearby river.

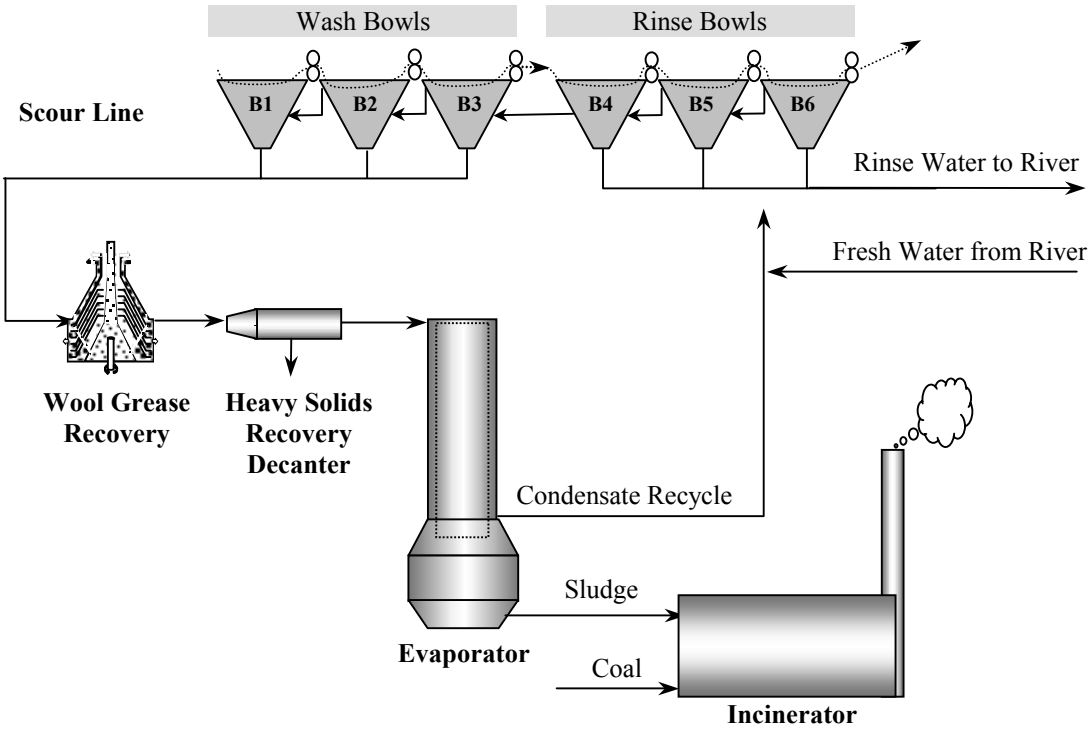


Figure 4.9 Case study 3, scour and effluent treatment plant.

In the plant under study, the flow of rinse water used in the scour is typically ten to twenty times the flow used in the wash section. Due to this large flow of rinse water the typical concentration of contaminants being discharged to the environment are relatively low:

Table 4.3 Case study 3, typical rinse water characteristics

BOD_5	100 – 200 mg/L
SS	300 – 400 mg/L
Wool Grease	50 – 150 mg/L

Each of the compounds discharged to river as in Table 4.3 are constrained by the local regulatory authority to a kg/day limit; for example, total suspended solids discharged (Concentration x Flow) must not exceed a given number of kilograms per day. This prevents the consent holder from simply flowing more water through the process to dilute the effluent and thus stay under the discharge consent level (as often happens when discharge consents are expressed as a straight contaminant concentration).

A key benefit of using this type of process is the low operating cost due to the energy required for evaporation being provided by burning of the sludge produced by the evaporator. Despite these benefits, the process has experienced problems with operating in close proximity to a populated residential district. This has been due to periodic discharge of odour from the incineration system disturbing residents to the extent that closure of the plant has been threatened several times by public complaints made to the local regulatory authority.

Due to the low contamination levels in the residual effluent and energy self sufficiency of the evaporation-incineration plant, the process described is an extremely effective treatment system, well matched to the needs of both the scour and local regulatory authority. As the odour emissions, which are currently jeopardising the continued operation of the scour, only occur intermittently - apparently dependent on the sludge quality being fed to the incinerator / boiler - this case study highlights the ever-present difficulties in matching an ideal treatment system to a given effluent problem.

4.4 CASE STUDY 4

4.4.1 OVERVIEW

Local Discharge Consent:	Unrestricted, Cost basis only
Typical Actual Discharge:	Heavy effluent phase: COD: 60,000 – 100,000mg/L SS: 38,000 – 60,000mg/L (Rinse water contribution is negligible)
Approximate capital Expenditure on effluent treatment:	$NZ 500,000 (1990)
Technologies Used:	2 Stage Wool Grease Recovery Gravity Settling of Heavy Solids

4.4.2 PROCESS DESCRIPTION

Case study 4 details the operation of a typical New Zealand wool scour processing a wide range of cross bred fleece, merino and slipe wools. In the case of this installation there are no explicit limitations on the level of contamination that is present in the water that is discharged to the local trade waste sewer. The local regulatory authority however, closely monitors the quality of the water discharged, and the scour is charged an effluent discharge fee based on the BOD_5, SS, Wool Grease and Volume flow levels measured.

The site consists of a single scouring line with a single WRONZ style integrated heavy solids and wool grease recovery loop as shown in Figure 4.10:

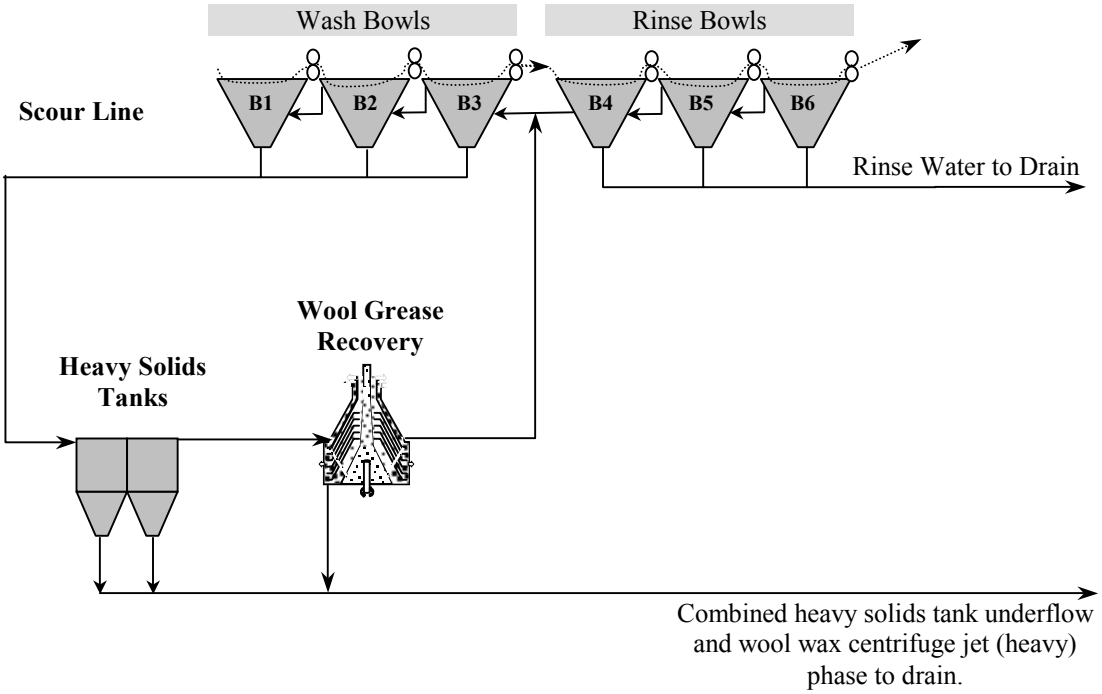


Figure 4.10 Case study 4, scour and recovery loop layout

The key advantage of the traditional WRONZ style recovery loop is that by combining the solids and wool grease recovery loops, there is a reduction in the quantity of hardware required (even if the loops are separated, the wool grease centrifuges still require some form of heavy solids protection upstream of them). In addition to this, if heavy solids tanks are used as the heavy solids recovery device rather than hydrocyclones, these tanks provide a buffer volume, which anecdotal evidence suggests aids in stabilising the flow of effluent into the wool grease recovery plant, which has in turn been observed to significantly improve the stability and effectiveness of the wool grease plant. (Turnbull 2001)

The biggest disadvantage of the WRONZ style combined recovery loop is that, due to the extreme difference between the physical characteristics of wool grease and heavy solids (usually sand or dirt), it becomes very difficult to optimise the loop for removal of both components. In particular, the liquor draw-off from the bowls to the recovery loop must be from the base of the hopper-bottomed wash bowls in order to facilitate solids removal from the bowl. It is immediately apparent that this draw-off point is the worst possible part of the bowl to draw off a stream rich in wool grease, which is lighter than water.

From an effluent treatment point of view, case study 4 illustrates the option of situating the scour in a location where there are low costs and minimal limitations imposed on the discharge of raw scouring effluent. This is a situation that is becoming more and more scarce throughout the world and, in respect of this, the managers of this plant are continuously evaluating and trailing potential effluent treatment systems for, as with the rest of the industry, it is now a case of when rather than if the local regulatory body will tighten its discharge consent limitations below the point at which the scour is currently discharging.

5 THE EXISTING ANDAR EFFLUENT TREATMENT PACKAGE

5.1.1 INTRODUCTION

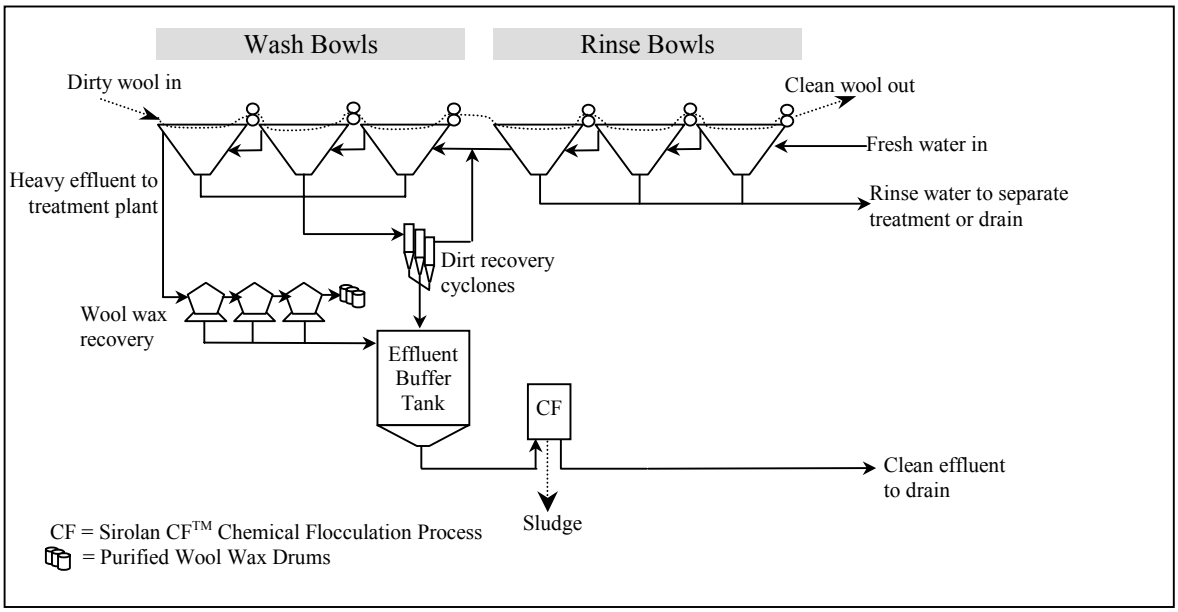


Figure 5.1 Wool scour with integrated effluent treatment plant

Figure 5.1 shows a typical scouring train of six bowls – in this case three wash bowls and three rinse bowls. Also shown are several water treatment and product recovery operations, such as wool grease recovery, solids recovery, and Sirolan CF. The three key factors that influence the contaminant loading passed on to any future down stream biological processing are:

- Effectiveness of wool grease recovery
- Water use in the scouring train
- Efficiency of Sirolan CF operation

As described in Section 1.3, much emphasis is already placed on recovering wool grease from the effluent stream, as this is a highly valued product. Most modern scours operate a two or three-stage wool grease recovery plant, and are regularly maintaining and updating the separation equipment to obtain maximum possible recovery of grease from the raw effluent.

The optimisation of water use in the scouring train is strongly dependent on regional factors, with total water use in the scour ranging from 6 to over 35 litres per kg of greasy wool

processed. In order to minimise the flow being sent on for further treatment, technologies such as separate dirt recovery loops (Figure 5.1) are frequently implemented.

5.1.2 SIROLAN CF

This study is based on the biological treatment of effluent pre-treated by the Sirolan CF chemical flocculation system. Due to the relatively recent commercialisation of this process, this pre-treatment system was judged to be the key up-stream process left open to further optimisation and improvement.

5.1.2.1 Theory of Coagulation – Flocculation

The Sirolan CF process works by dosing an acid (usually sulphuric) into the heavy flow-down effluent until the surface charge of the suspended particulates corresponds to that of the active sites of the polymer flocculent used. The pH-adjusted effluent is then dosed with a cationic polyelectrolyte flocculent, which binds with the appropriately charged suspended particles and wool grease droplets.

At this point it is useful to look at the forces involved in determining the stability (or lack there of) in disperse systems.

As the forces of attraction and repulsion between particles are generally considered to be the summation of interactions between the molecules in the particles (Everett 1988), we must begin with molecular interaction. While some molecules or atoms are attracted to others by ionic, covalent, or hydrogen bonding forces, all molecules are attracted to each other by van der Waals forces (Sevile *et al.* 1997). Van der Waals forces arise from fluctuations in the electron cloud distribution around the molecule creating a temporary dipole (or charge imbalance), which then induces a corresponding charge imbalance in the neighbouring molecules.

The net effect of this force can be illustrated by looking at how the electrical force between two hydrogen atoms interacts causing attraction or repulsion at different distances of separation:

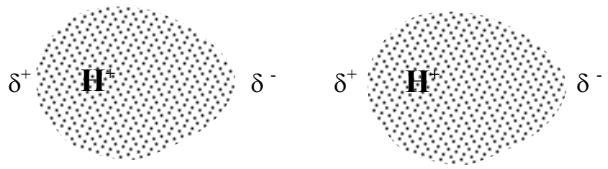


Figure 5.2 Instantaneous dipole between two hydrogen atoms

The neighbouring δ- and δ+ charges then exert an attractive force in each other and the subsequent instantaneous dipole moment of attraction between two hydrogen atoms is:

$$P_1 = a_0 e \qquad (1)$$

Where:

a_0 = Bohr radius of ground state orbital

e = electron charge

The subsequent potential energy of attraction between the two dipoles at distance of separation r is:

$$\Delta G^{att} = \frac{\alpha\, a_0^2 e^2}{(4\pi\,\varepsilon_0)^2 r^6} \qquad (2)$$

Where:

V_A = Potential energy of attractive interaction

α = polarisability of the atom / molecule

ε_0 = permitivity of free space

r = separation distance

And for a given atomic species the term $\frac{\alpha\, a_0^2 e^2}{(4\pi\,\varepsilon_0)^2}$ is constant and can be represented as the positive constant C_6 such that Equation (2) becomes:

$$\Delta G^{att} = \frac{C_6}{r^6} \qquad (3)$$

As two molecules come closer together however the negatively charged electron clouds begin to interact and subsequently repel each other. So long as the outer electrons are in a non-bonding orbital, the repulsive force generated effectively becomes infinite once the electron

clouds merge, and is generally expressed in a simplified form corresponding to Equation (3) (Everett 1988):

$$\Delta G^{rep} = \frac{C_{12}}{r^{12}} \quad (4)$$

Where C_{12} is a positive constant for a given molecular species.

To determine the overall variation of potential energy with distance of separation between the two molecules, the summation of the attractive and repulsive forces are taken:

$$\Delta G = \Delta G^{rep} - \Delta G^{att} = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6} \quad (5)$$

Note: in this case the convention is followed that attractive forces are negative and repulsion forces are positive.

This relationship is illustrated graphically in Figure 5.3 below:

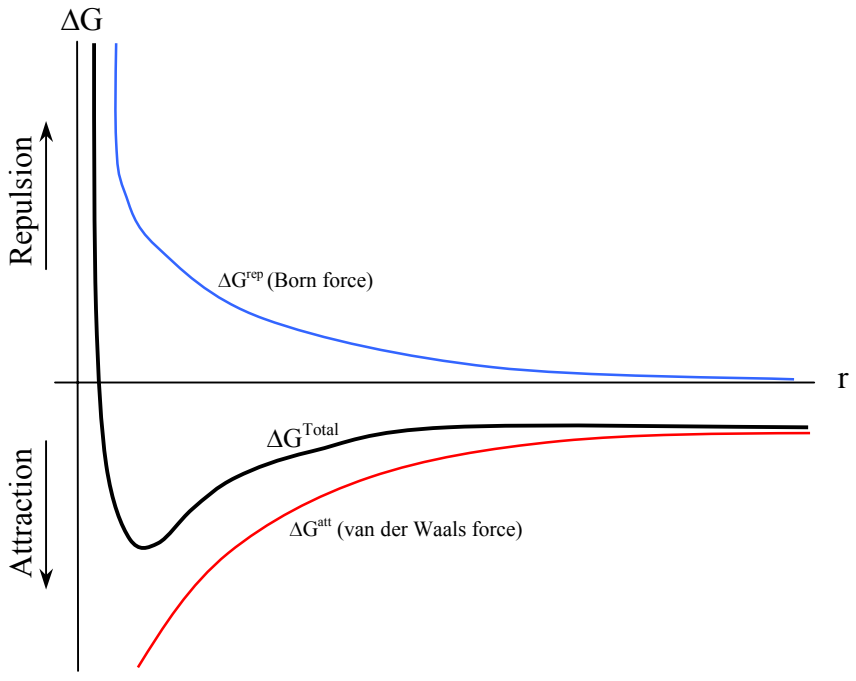


Figure 5.3 Variation of intermolecular force with separation distance

The curve for total potential energy has the following key features:

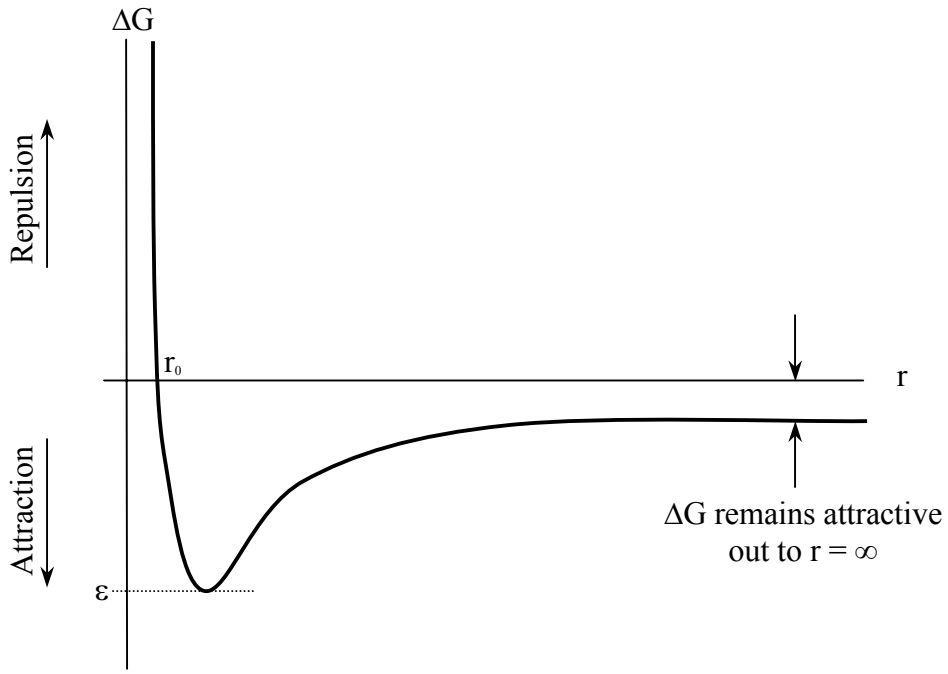


Figure 5.4 Features of the potential energy curve

Using the depth of the potential well (ε) and the distance at which the potential becomes zero (r_0) in Figure 5.4, Equation (5) can be re written as:

$$\Delta G = 4\varepsilon \left(\frac{r_0}{r^{12}} - \frac{r_0}{r^6} \right) \quad (6)$$

The standard method of determining the potential energy of particulate interactions is to assume that the interaction energy of the particles is the sum of every molecule in each particle interacting with every particle in the other molecule (Everett 1988; Sevile *et al.* 1997; Cooper 1999).

Cooper (Cooper 1999) gives the following approximations for applying this molecular interaction model to particulate interaction:

The attraction between a molecule and solid slab can be determined by summing the interaction of the free molecule with all the molecules in the slab.

$$\Delta G = -\sum_{i=1}^{n} \frac{C_6}{r_i^6} \quad (7)$$

Where n is the number of particles in the slab, and due to the large distances involved the Born force (due to electron cloud interaction) is considered negligible.

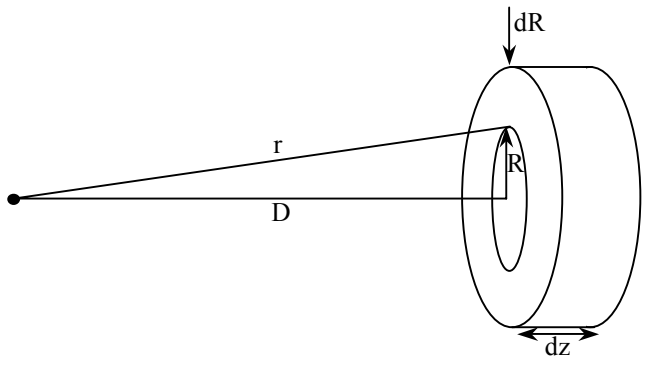


Figure 5.5 Interaction of a single molecule with a slab.

For a section of slab of depth dz, and thickness dR with a single molecule at distance D (Figure 5.5), this summation can be expressed as the integral of the energy of all the atoms in the slab with respect to slab depth and thickness:

$$\Delta G = -C_6 \rho' \int_0^\infty \int_0^\infty \frac{2\pi R}{r^6} dR\, dz \qquad (8)$$

Where:

Number of atoms in a small volume of slab = ρ'dV

dV = small element of slab volume = 2πR dR dz

ρ' = density [molecules / unit volume of particles]

And since from Figure 5.5 $r^2 = (D + z)^2 + R^2$ Equation (8) becomes:

$$\Delta G = -C_6 \rho' \int_0^\infty \int_0^\infty \frac{2\pi R}{\left((D + z)^2 + R^2\right)^3} dR\, dz \qquad (9)$$

$$\therefore \quad \Delta G = -\frac{\pi C_6 \rho'}{6 D^3} \qquad (10)$$

If the particles can be thought of as two infinitely large flat plates (which in comparing a particle surface to the size of a single molecule can be a viable assertion) then the attraction

energy per unit surface area can be determined by further integrating Equation (10) with respect to D from D = D to D = ∞:

$$\Delta G = \int_D^{\infty} -\frac{\pi C_6 \rho'}{6 D^3} dD \qquad (11)$$

$$\therefore \Delta G = -\frac{A_H}{12 \pi D^2} \qquad (12)$$

Where:

A_H = Hamaker constant $A_H = \frac{3}{4} h\nu \alpha^2 \pi^2 \rho'^2$

h = Planck's Constant (6.63×10^{-4}Js)

ν = Characteristic frequency corresponding to the first ionisation potential of the molecule

α = Polarisability of the molecule

ρ' = Number of molecules in a unit volume of particles

It can be seen from a comparison of Equations (3) and (12) that the attractive force between particles falls off much more slowly with distance than the equivalent force between individual atoms or molecules.

For two spherical particles of equal radius (a), distance H apart the attraction energy can be approximated to:

$$\Delta G = -\frac{A_H a}{12 H}\left[1 + \left(\frac{3}{4}\right)\frac{H}{a} + higher \quad terms \right] \qquad (13)$$

So long as the particles are close together ($H \ll a$) (Everett 1988).

The above theory assumes instantaneous interaction between neighbouring molecular or atomic dipoles. If the distance between the particles is large (in effect > 10nm is considered large) then in the time taken for a change in the electric field of one molecule to reach the other, the state of the neighbouring molecule may have changed. A more robust theory has been developed by Lifshitz (Lifshitz *et al.* 1980) that takes account of this effect, also without requiring the assumption that the interactions of larger particles are merely the sum of the molecular interactions. The Lifshitz theory however involves implementation of quantum

field theory in calculating the Hamaker constant (which actually turns out to vary somewhat under different conditions), the details of quantum field theory are considered beyond the scope of this work. In general, the retardation effect of the time delay between the particles is considered to add one extra order proportionality to the dependence of potential energy on distance between the particles, i.e. in Equation (12) ΔG becomes proportional to D^{-3} rather than D^{-2} when D > 10nm (Cooper 1999).

The general result of the inter-particle forces summarised above is that even when separated by significant distance, the inter particulate forces remain attractive. The most thermodynamically stable state for particle dispersions to be in is therefore for all of the particles to coalesce into larger particles. Given this result, how then is it possible to obtain the apparently stable particulate dispersions that are encountered in real systems, and which are of great interest to those engaged in water treatment activities?

Although the dispersed system is thermodynamically unstable it can be considered metastable as the system is under kinetic rather than thermodynamic control (Cooper 1999). This is due to an overriding phenomenon that commonly occurs in aqueous systems.

Particulate matter suspended in aqueous solution develops an electrical double layer, or surface charge, which gives rise to repulsive forces between particles. This hinders the collision between particles required for the particles to join together into larger masses, which can then be removed from solution by sedimentation.

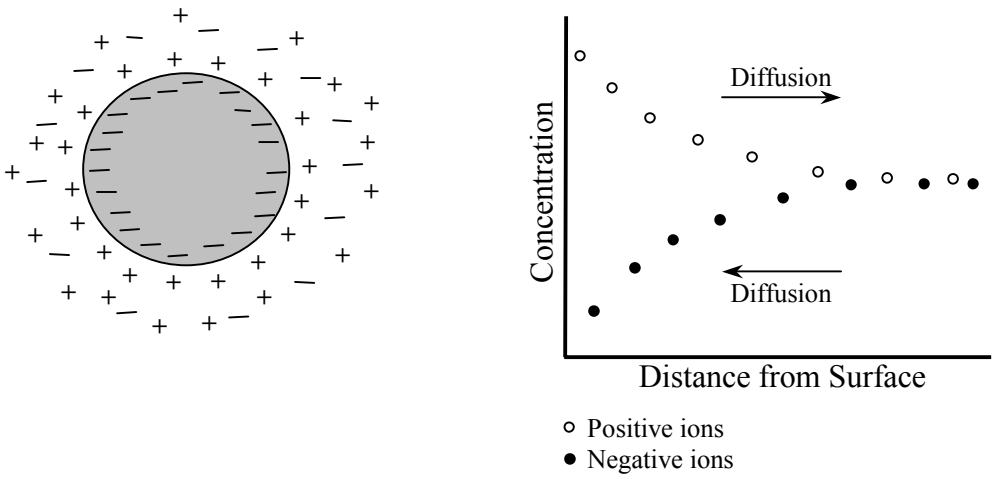


Figure 5.6 Electrical double layer formation – Adapted from Kilduff (Kilduff 1999)

When the ionic strength of the solution is increased (such as is achieved by adding a strong acid to the system) the thickness of this electric double layer (known as the Debye length) is rapidly decreased. At a certain ionic strength, the Debye length falls to zero, and the surface charge (or zeta potential) of the particle is also reduced to zero. At this point there is no repulsive force to hinder approach and subsequent collision of multiple particles into a larger coagulated mass.

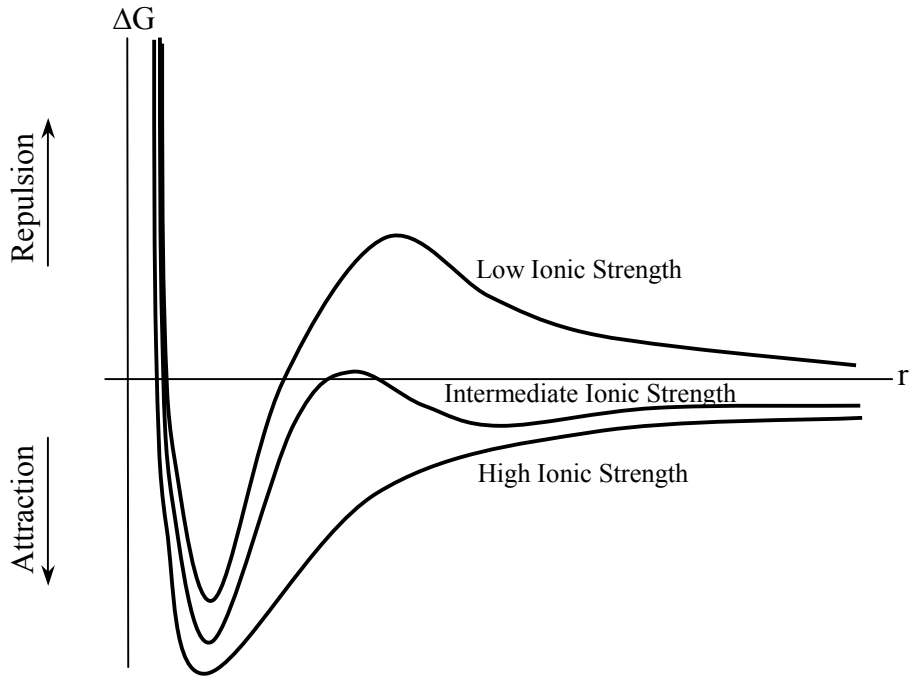


Figure 5.7 Effect of electrolyte ionic strength on attraction energy. ***Adapted from Cooper (Cooper 1999).***

Low ionic strength – Strong electrical double layer forms and subsequent dispersions are stable due to net repulsion between particles.

Intermediate ionic strength – Due to some compression of electrical double layers, the van der Waals attraction force is offset at some distances and not others. Dispersion may be stable or unstable.

High ionic strength – electrical double layer is compressed to the point of being entirely neutralised, and van der Waals attraction force is the dominating interparticle force. Dispersions are subsequently unstable with collisions leading to particle coagulation.

This phenomenon is particularly relevant to proteins, as their surface charge is highly dependent on pH of the medium in which they are suspended. Also in detergent stabilised systems the detergent encased colloids are further stabilised by formation of an electrical double layer on the hydrophilic shell of the detergent micelle (Atkins 1982).

Kilduff also describes the process of physical adsorption of H^+ ions onto the surface of the suspended particles, which under optimal surface coverage can reduce the zeta potential to zero. Higher concentrations of H^+ ions in solution however can lead to charge reversal and re-stabilisation of suspension by a positive repulsive charge on the suspended molecules. Dose rate of acid in such systems must therefore be tightly controlled (Kilduff 1999).

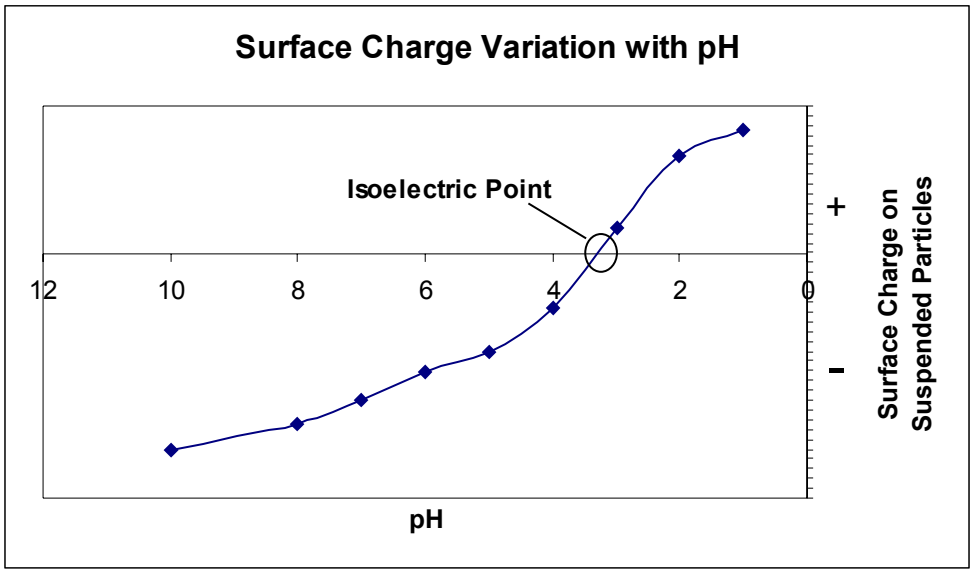


Figure 5.8 - Effect of pH on particulate solids in the effluent

Once the suspension stabilising electrical double layer has been suppressed or neutralised by hydrogen atom adsorption and the increased ionic strength of the solution, a polymeric flocculent is often added to the suspension in order to attract the destabilised particles together into even larger groups known as flocs. One of the most common polymers used in water treatment applications (including the wool scouring industry) is polyacrylamide. This is a long chain polymer, which is commercially available in a range of molecular weights and charge densities (including anionic, non-ionic, and cationic)

The commercially available products are generally classed as one of the following size categories:

Table 5.1 Categorisation of polymer flocculent molecular weight

Low Molecular Weight	$< 10^5$ g/mol
Medium Molecular Weight	$10^5 – 10^6$ g/mol
High Molecular Weight	$1x10^6 – 5x10^6$ g/mol
Very High Molecular Weight	$> 5x10^6$ g/mol

The factor that most influences the activity of the polymer in disperse suspensions however is the charge of the active units distributed along the length of the polymer chain. A straight polyacrylamide polymer chain made up of repeating units of the acrylamide monomer is non-ionic, and does not have any charged groups (Barvenik 1994):

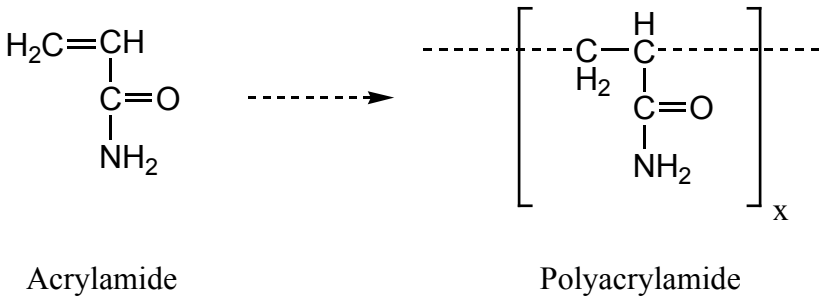


Figure 5.9 Non-ionic polyacrylamide polymer

Alternatively, by hydrolysis of differently charged groups into the polymer chain, cationic or anionic polyelectrolyte polymers can be formed with charged groups distributed along their length at a pre-determined frequency (the ratio of y/(x+y) in Figure 5.10):

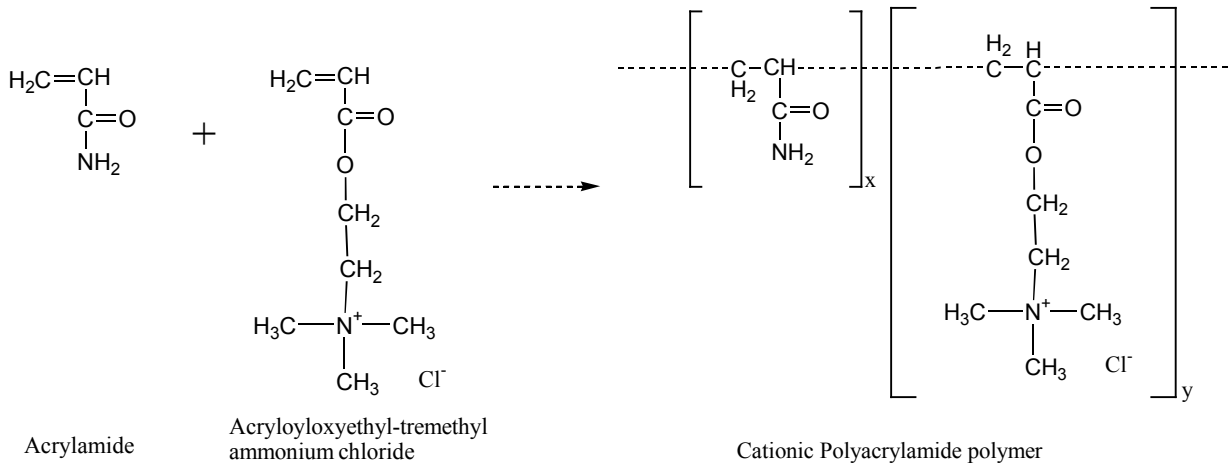
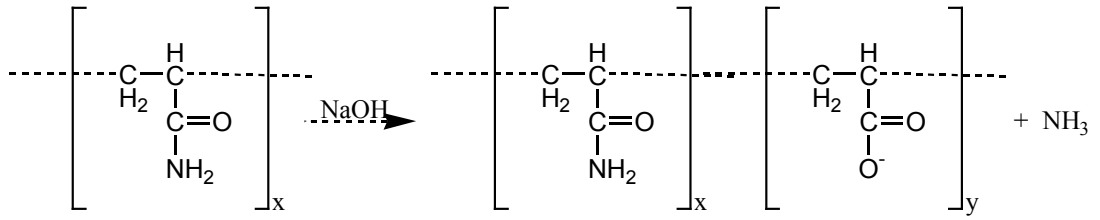


Figure 5.10 Cationic polyacrylamide polymer



Non-ionic Polyacrylamide polymer — Anionic Polyacrylamide polymer — Ammonia

Figure 5.11 Anionic polyacrylamide polymer

In the later polyelectrolytic cases (Figure 5.10 and Figure 5.11) where the polyacrylamide chain is made up of a combination of acrylamide monomers and charged monomers, the ratio of charged units (y) to uncharged acrylamide monomers (x) determines the charge density of the overall polymer (Barvenik 1994). The polymers used in the Sirolan CF flocculation process are high molecular weight, high cationic charge density polyacrylamides (Figure 5.10).

When the long polyelectrolytic polymer chains in solution come into contact with suspended particulate matter, the charged sites of the polymer chain attach to matching ionic sites on the surface of the suspended particles. Polymers such as polyacrylamide, which have polar groups (C=O on the acrylamide monomer) as part of the polymer chain are also capable of hydrogen bonding to the particle surface when electrical double layer repulsion is sufficiently suppressed (Gregory 1978). The length of the polymer is such that the chain is able to bond to multiple particles in solution, thus bridging them together into macro particles, which under ideal conditions can measure several millimetres in diameter.

It is often observed in flocculation systems that there occurs an optimum polymer concentration for flocculation, both above and below which the level of flocculation is significantly reduced. This principal is illustrated in Figure 5.12 (Michaels 1954) below:

(a) Insufficient Polymer – Not all particles collected

(b) Optimum Polymer dose – All particles are bound together

(c) Too much Polymer– Each particle becomes so tightly bound with polymer that there are no adsorption sites left on particles for inter-particle bonding of polymer

Figure 5.12 'Bridging' flocculation between suspended particles – effect of polymer dose

As can be seen by Figure 5.12, the optimum concentration of polymer required to bind together all particles is proportional to the surface area of particles available for adsorption of the polymer, and therefore to suspended solids concentration.

At low suspended solids concentrations, using the same polymer dose rate as is used at higher solids concentrations is not merely a waste of polymer, but may actually cause the flocculation process to fail to perform at the required level (Figure 5.12c).

Due to their long chain lengths (up to 1μm for high molecular weight polyacrylamides) great care must be taken in the mixing of polymer solutions. While polyacrylamide powder must be wetted out completely and then exposed to a brief period of high shear mixing to obtain initial dispersion in water (Gregory 1978), any extended exposure to high shear mixing will degrade the polymer due to cleavage of the relatively long polymer chains into shorter, less effective units (Abdel-Alim *et al.* 1973).

While Barvenik (Barvenik 1994) reports that solutions made up from dry polyacrylamide powder require 30 – 60 minutes of aging prior to use, these bulk solutions must not be stored for excessive periods (~two or more days) once hydrated as they have been widely reported to be subject to 'aging' effects causing gradual deactivation of the polymer activity (Gregory 1978). These bulk solutions of polyacrylamide are generally made up to strengths of less than 0.5% polymer powder in water due to the excessive viscosities of solutions stronger than this.

It is widely reported that the three main types of collision mechanisms for suspended particulate matter are: by random Brownian motion (perikinetic), by differential settling of the solids, and by bulk fluid motion or turbulence (orthokinetic) . The level of turbulence in the fluid is the easiest one of these mechanisms to control, as this can be induced by simply stirring the liquor [Kilduff, 1999 #273].

Therefore, upon contacting the bulk polymer solution with the destabilised solids suspension, a high degree of turbulent mixing is required such that there are sufficient particle – particle and particle – polymer collisions to facilitate complete flocculation. Once particles begin flocculating however, the shear force exerted upon them should be limited least the flocs be broken up again and the solids redispersed in the aqueous phase. Tapered mixing is often employed in order to achieve the optimum level of particle contacting without excessive shearing of the resultant flocs. Oldshue (Oldshue 1983) recommends the use of baffled channels for achieving tapered mixing. Well designed static mixers have been observed by the author to also give excellent results.

The level of mixing in a given system is often expressed as the shear rate (or G-factor) of that system (Gregory 1978; Biickert 1996; Cooper 1999; Visvanathan 2000):

$$G = k\sqrt{\frac{W}{\mu V}} \quad (14)$$

Where:

G = Shear rate [s^{-1}]

W = Power dissipated [W]

μ = Viscosity [Pa.s]

V = Volume of mixer [m^3]

k = Constant based on mixer type (See Table 3.3 in Visvanathan (Visvanathan 2000) for values)

The power dissipated by a static mixer can be calculated as:

$$W = gQh \quad (15)$$

Where:

W = Power dissipated [W]

g = specific weight of water [N/m^3]

Q = Flow rate through mixer [m^3/s]

h = dynamic head loss over mixer [m]

Typical values of shear rate used in flocculation applications are 100 – 200 s^{-1}. (Visvanathan 2000)

5.1.2.2 The Sirolan CF Process

The entire Sirolan CF chemical flocculation process is achieved 'in-line' by use of direct chemical injection into static mixers in the effluent pipeline. The flocculated effluent is sent to a decanter centrifuge where the solid and grease fractions are separated from the bulk liquid phase into a single sludge and dewatered.

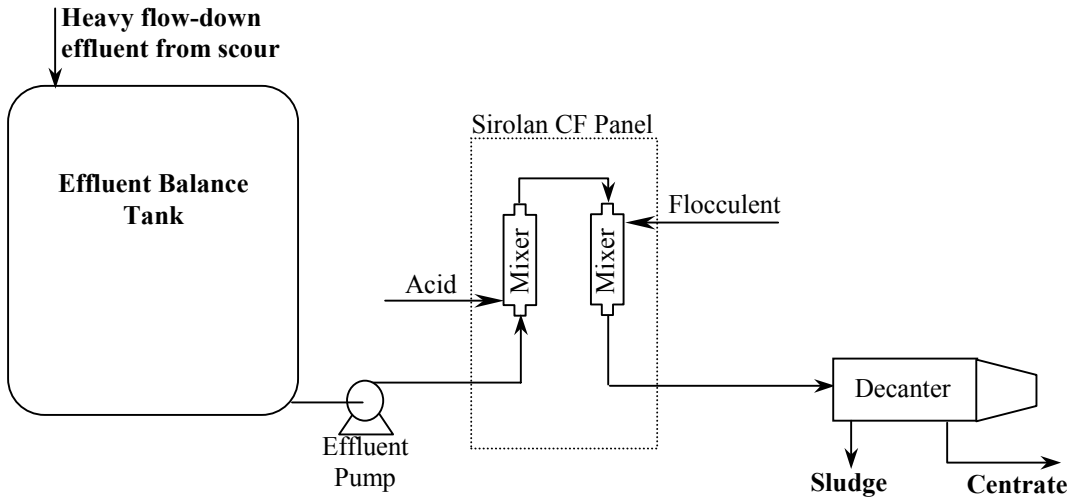


Figure 5.13 – The Sirolan CF process

The Sirolan CF process typically gives a 55 – 65% dry sludge, while removing 96% – 99.9% of the effluent suspended solids, and 90%+ of the residual wool grease that has escaped the recovery centrifuges. A summary of effluent characteristics and process performance is given in Table 5.2 and Table 5.3 below:

Table 5.2 Heavy flow-down effluent before and after Sirolan CF

	BOD_5 [mg/L]	COD [mg/L]	Dirt [mg/L]	Grease [mg/L]
Scour heavy flow-down (NZ Scour)	35,000 – 45,000	60,000 – 150,000	25,000 – 60,000	10,000 – 30,000
Scour heavy flow-down (Aust. Scour)	12,000 – 30,000	40,000 – 75,000	18,000 – 65,000	9,000 – 21,000
Sirolan CF Centrate (NZ Scour)	3,500 – 8,700	12,000 – 25,000	220 – 2,000	200 – 3,000
Sirolan CF Centrate (Aust. Scour)	2,400 – 5,500	8,000 – 15,000	400 – 2,200	100 – 3,500

Table 5.3 Typical Sirolan CF sludge properties

	Total Solids $\%_{w/w}$	Dirt $\%_{w/w}$	Grease $\%_{w/w}$
Sirolan CF Sludge (NZ Scour)	55 – 68	25 – 45	10 – 26
Sirolan CF Sludge (Aust. Scour)	44 – 62	24 – 47	12 – 28

The operating parameters under which the Sirolan CF process runs (primarily acid and polymer dosing rates) are highly dependent on the feed effluent quality. Effluent quality parameters such as solids and grease loading not only vary strongly from country to country as shown in Table 5.2 but also from plant to plant and from day to day within any given plant. For instance, a scour washing slipe wool one day and Australian merino fleece the next could easily experience a 100% increase in the level of suspended solids in its heavy flow-down effluent between the two batches.

Analysis of results gathered by the CSIRO (Bateup *et al.* 1996) shows a general trend towards increasing levels of both particulate solids and wool grease in the centrate of the Sirolan CF process when a high wool grease concentration is present in the feed liquor.

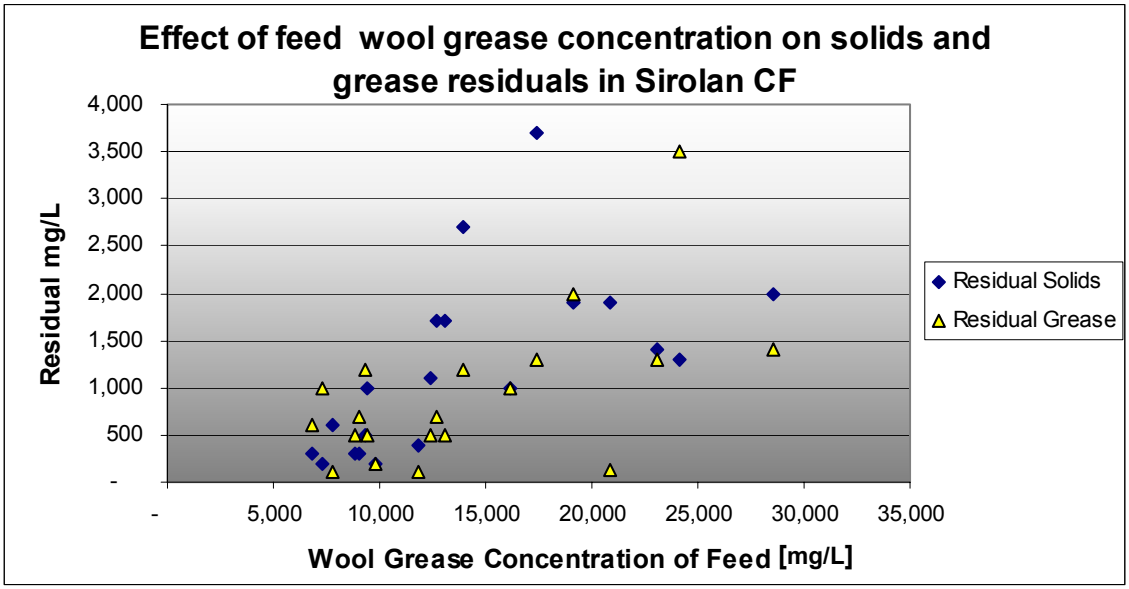


Figure 5.14 Effect of feed wool grease concentration on solids and grease residuals in Sirolan CF

Also shown by this analysis to be of significance was the ratio of particulate solids to wool grease in the feed liquor. As the ratio of particulate matter to wool grease in the feed effluent increased, the level of residual wool grease and particulate matter in the centrate tended to drop. This trend has also been observed repeatedly by the author when operating the process on New Zealand scouring effluent.

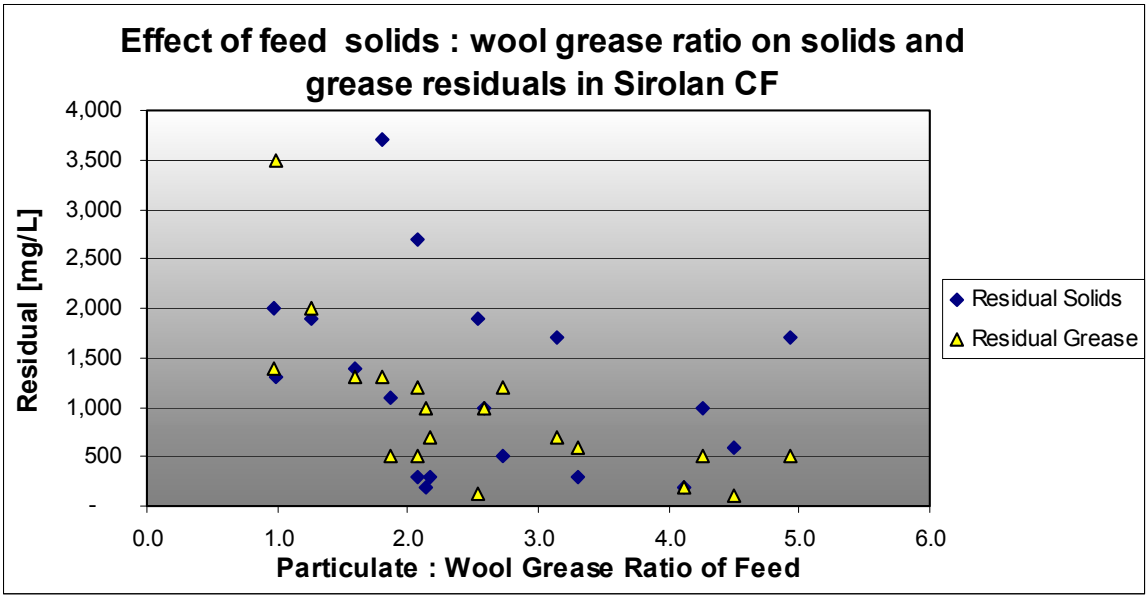


Figure 5.15 Effect of feed solids :wool grease ratio on solids and grease residuals in Sirolan CF

Again this result brings to the forefront the importance of optimising wool grease recovery prior to discharging the scour liquor to the effluent treatment plant. It also however raises the interesting factor of solids level in the feed liquor. This relationship suggests that if the particulate solids concentration of the feed to the Sirolan CF system is increased, then the quality of the resultant centrate will actually improve.

In initial trials with the Fairlie Wool Scour Sirolan CF pilot plant (Savage 1999), the dependence of Sirolan CF centrate quality on feed suspended solids was tested by altering the ratio of feed from the heavy solids loop (underflow of a gravity settling tank system) and the jet phase of the wool grease recovery plant where the majority of un-recovered wool grease can be found.

The results of these tests are presented in Figure 5.16 overleaf.

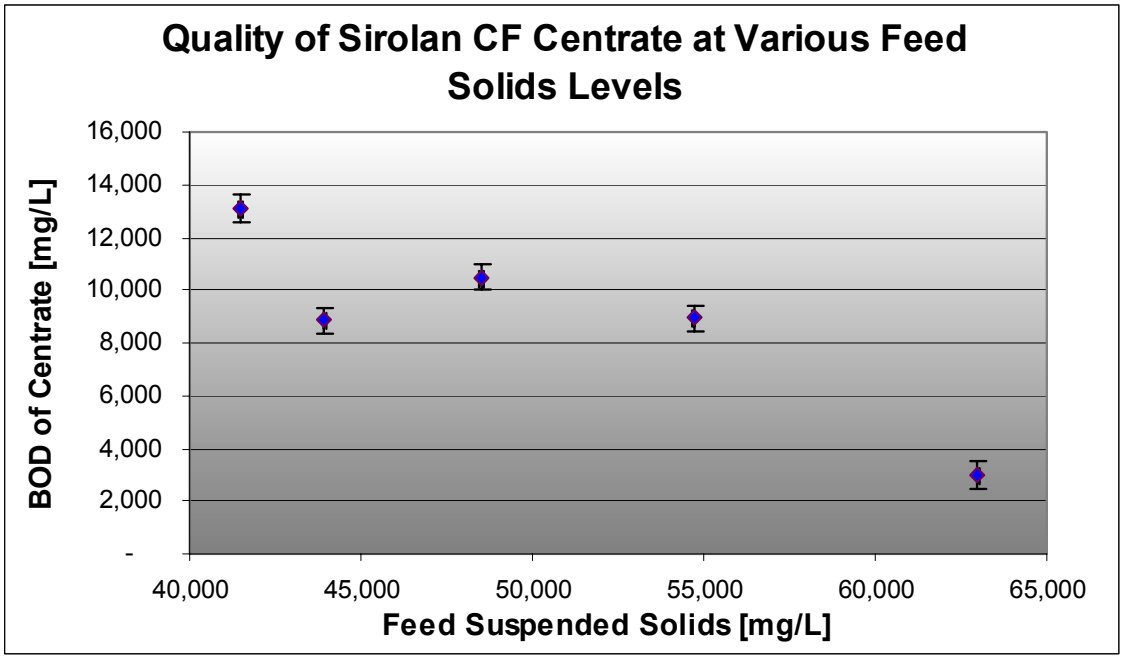


Figure 5.16 Quality of Sirolan CF centrate at various feed solids levels

Biological Oxygen Demand (BOD_5) was used in this case as a parameter representing centrate quality, as it is representative of the combined suspended solids, wool grease and dissolved organic compound concentration. BOD_5 is also one of the most common parameters used for determining the cost basis for discharge of trade waste to sewer.

The relationship shown in Figure 5.16 corresponds well with that suggested by Figure 5.14 and Figure 5.15. It can thus be reliably concluded that for both Australian and New Zealand wool an increase in the suspended solids concentration fed to the Chemical Flocculation system gives a corresponding improvement in the quality of the resulting centrate from the system.

Three key methods of increasing the proportion of solids in the feed were identified.

1. Install a heavy solids recovery loop and feed the solids rich underflow of this to the Sirolan CF system.
2. Recycle a portion of the solids from the Sirolan CF decanter to the feed of the Sirolan CF system.
3. Allow the feed tank to the Sirolan CF system to develop anaerobic microbiological growth prior to processing with Sirolan CF.

Option 1. above is illustrated by the use of dirt recovery hydrocyclones in Figure 5.1. By using a dirt recovery loop, the heavy solids in the wash section of the scour can be removed and most of the water returned to the scour. This reduces the overall flow-down from an average scour by approximately 25%, with an accompanying 25% increase in the overall solids concentration fed to Sirolan CF.

Option 2. has not been widely investigated and may entail problems with the quantity of wool grease re-introduced into the system. As shown by Table 5.3 above, up to half the dry weight of the sludge can be made up of solvent extractables (wool grease and detergent), which have been shown to be detrimental to the chemical flocculation process.

The most successful method of feed improvement was found to be Option 3. which is discussed in detail in the next section.

5.2 ANAEROBIC PRE-TREATMENT OF SIROLAN CF FEED EFFLUENT

When left to stagnate in the absence of oxygenation, wool scour liquors turn black and begin to give off the characteristic odour of hydrogen sulphide within 12 hours. The black coloration has been observed to be due to the formation of insoluble ferric sulphides from the combination of iron oxides from the mineral dirt fraction of the effluent and sulphide ions from either residual depilatory on slipe wool, or the sulphur rich keratin in the residual wool fibres in the effluent (McLaughlin *et al.* 1992). The formation of these insoluble iron sulphide particles was shown to proceed unhindered in the absence of both depilatory chemicals and anaerobic biological growth, requiring only a reducing environment, which was brought about by lack of dissolved oxygen in the wool scouring effluent.

The ease with which heavy wool scouring effluent develops anaerobic bacterial growth, if left to stagnate under ambient conditions, has led many a researcher to attempt the development of anaerobic wool scour effluent treatment technologies. Many of these applications of anaerobic treatment processes utilised in the wool scouring industry have been reviewed by Stewart (Stewart 1988). In this review, attempts by various researchers to apply anaerobic digestion technologies including Upward flow Anaerobic Sludge Blanket (UASB), anaerobic filters, and traditional mixed tank systems are outlined. The only application Stewart details where this has been commercially successful is in the use of a 20-day hydraulic residence time, conventional mixed reactor where heavy flow-down liquor mixed with domestic effluent is treated. The long residence time required for anaerobic treatment is also emphasised by research carried out at Murdoch University in Western Australia (Isaac *et al.* 1991). This work reports a minimum of 30-day hydraulic retention time for 50% reduction in COD of heavy wool scouring effluent by anaerobic digestion.

Recently the emphasis of study into anaerobic treatment systems for application in this field has shifted to short term, partial digestion treatments that do not actually seek to remove the organic loading of the effluent stream by anaerobic digestion alone. In these recent applications, primarily carried out at the Murdoch University Institute for Environmental Science, the focus has shifted to using the anaerobic process as a pre-treatment to destabilise the effluent prior to further chemical coagulation and / or flocculation (Lapsirikul *et al.* 1994a; Lapsirikul *et al.* 1994b; Lapsirikul *et al.* 1994c; Charles *et al.* 1996; Mercz *et al.* 1997).

Although the initial anaerobic bacterial growth generates a significant increase in suspended solids concentration of the feed to Sirolan CF, the effect of this increase (Figure 5.16) cannot alone account for the improved centrate quality observed after anaerobic pre-treatment. The effects of particle coagulation, biological flocculation and wool grease separation by flotation are all relevant factors. Researchers at Murdoch University (Mercz *et al.* 1997), focused on optimising grease removal by bioflocculation in the anaerobic pre-treatment phase. With a 2-3 day anaerobic treatment they were able to provide upwards of 30% total grease removal. When combined with a second stage process where a polymer flocculent was added at 100 – 200ppm concentration, a 60 – 80% reduction of wool grease concentration was observed.

Previous studies (Lapsirikul *et al.* 1992) have attributed the destabilisation of the wool grease emulsion that occurs during anaerobic bioflocculation to partial microbial degradation of the hydrophilic ethoxylate side chains of the wool scouring detergent (nonylphenol ethoxylate). The resultant destabilised grease droplets coalesce and float to the surface, while the anaerobic biomass flocculates the particulate matter in solution. Later work has confirmed that the biomass formed by the anaerobic bacteria has no physical or chemical flocculation properties once sterilised (Lapsirikul *et al.* 1994b), thus verifying that the grease separation is indeed biologically driven.

It is commonly acknowledged that at high loading rate, continuous flow anaerobic reactors are very difficult to operate due to the constant high substrate level overloading the anaerobic culture leading to imbalance between fermentation and methanogenesis with resultant acidification and death of the reactor contents (Isaac *et al.* 1991; Inanc *et al.* 1999). The volatile fatty acids (such as propionic acid) that cause this phenomenon are end products of fermentation. In contrast to carbohydrates and proteins, the lipids in wool grease are already highly reduced compounds and can therefore not be further reduced by fermentation to the volatile fatty acids that so commonly cause the demise of high rate anaerobic treatment processes. It is therefore proposed that a high loading rate anaerobic reactor processing a high lipid content effluent such as wool scouring waste will not suffer from this problem. (Isaac *et al.* 1991).

5.2.1 METHOD ANAEROBIC PRE-TREATMENT OF SIROLAN CF LIQUOR

In order to identify and evaluate the effect of allowing the feed to the Sirolan CF chemical flocculation process to develop anaerobic growth as detailed in section 5.2, several independent investigations were carried out.

Over a 2 year period of pilot plant operation and evaluation of the Sirolan CF process at Fairlie Wool Scour, Timaru (FWS) the small ~1m^3 feed tank from which the feed to the Sirolan CF process was drawn (Figure 5.17) was occasionally allowed to sit stagnant for a day or more. During this time the effluent developed significant anaerobic biological growth. When the process was restarted the centrate produced from this anaerobic feed was analysed for suspended solids and BOD_5 levels.

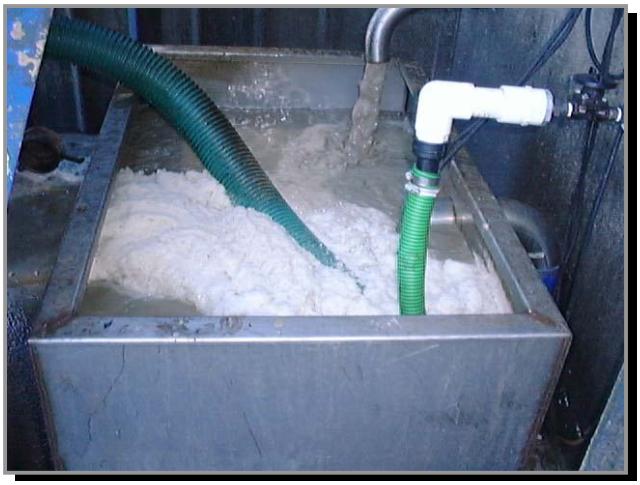


Figure 5.17 Sirolan CF pilot plant feed tank

5.2.1.1 Acid Consumption Analysis

In the process of this investigation, the acid consumption in the Sirolan CF process at any given time was monitored by use of a graduated 20L vessel from which the acid was drawn and the totalising function of the effluent magnetic flow meter, which tracked the total effluent flow into which the measured volume of acid was dosed. It was observed that, on average, a significantly reduced level of acid consumption was encountered when operating with the anaerobic effluent feed stock.

In order to eliminate the influence of daily effluent quality variation from the results obtained, a controlled experiment was carried out to isolate the effect of allowing the effluent to develop anaerobic growth from other day to day variations in the effluent makeup.

In this investigation two identical 200mL samples of heavy flow-down effluent were taken and analysed for pH response to sulphuric acid addition. The first sample was taken from the surface of the Sirolan CF feed tank and immediately tested for pH response by incrementally

adding dilute sulphuric acid while monitoring the pH of the solution. This models the acid consumption of the Sirolan CF process as normally operated.

A second sample was taken at the same time and place as the first, then allowed to stagnate unstirred for 14 hours to enable anaerobic growth to develop. After 14 hours, the sample was shaken and tested for pH response as described above.

5.2.1.2 Commercial Scale Confirmation of Results

In order to confirm the observations of reduced acid use and improved centrate quality with combined anaerobic bio-flocculation and chemical flocculation, a second controlled experiment was carried out at a New Zealand wool scour, which was trialing a full scale Sirolan CF process. The wool scour in question had a $30m^3$ 'off spec' effluent tank which was available for use as an anaerobic storage tank prior to the Sirolan CF process.

After the trial Sirolan CF process was commissioned and had been running almost continuously in standard configuration for two weeks, a trial was carried out to investigate the influence of anaerobic pre-treatment on the effluent quality and acid consumption.

In this case both the acid and effluent lines were fitted with EMC electromagnetic flow meters, making assessment of acid / effluent ratios both easier and more accurate. The results obtained indicate an average dosing rate [$L_{acid}/m^3_{effluent}$] over one hour of operation.

To carry out the experiment, the centrate quality and acid consumption of the Sirolan CF process were recorded under normal operating conditions. After these measurements had been taken, $30m^3$ of raw heavy flow-down feed-effluent was then re-directed to the anaerobic storage tank where it was held for a period of 28 hours (without anaerobic seeding) to allow anaerobic growth and subsequent bioflocculation to occur.

Figure 5.18 30m^3 off spec tank

Figure 5.19 Full scale Sirolan CF process used in trial

The contents of the anaerobic storage tank were then fed through the Sirolan CF process and the acid consumption and centrate quality measured.

5.2.2 RESULTS - ANAEROBIC BIO-FLOCCULATION

5.2.2.1 Initial Observations

When the feed tank to the pilot plant Sirolan CF unit installed at Fairlie Wool Scour was allowed to develop anaerobic growth (for example when it was left stagnant over a weekend) prior to passing through the CF unit, a considerably higher level of effluent treatment was achieved.

Feed Type	SS removal	BOD_5 removal
Crossbred fleece effluent	94.3%	65.2%
Crossbred fleece effluent	96.3%	67.4%
Crossbred fleece effluent	86.7%	33.3%
Anaerobic feed liquor	**98.7%**	**71.1%**
Heavily anaerobic, feed liquor	**99.3%**	**82.1%**

Table 5.4 Typical results from 1999 Sirolan CF trials at FWS

Under anaerobic conditions, the optimum pH of operation of the Sirolan CF process was observed to increase from the usual 3.3 to 4.2 – 4.6, a change that had serious implications for the chemical cost of dosing acid to the process. Tests were carried out on the pilot plant early in 2001 to quantify the saving in chemical cost to which this increase in pH would typically correspond to.

5.2.2.2 Chemical Consumption of Anaerobic Chemical Flocculation

From the controlled experiments detailed in Section 5.2.1.1, acid dose response curves were developed for the normal heavy flow-down and for the same effluent after 14 hours of storage under anaerobic conditions (Figure 5.20).

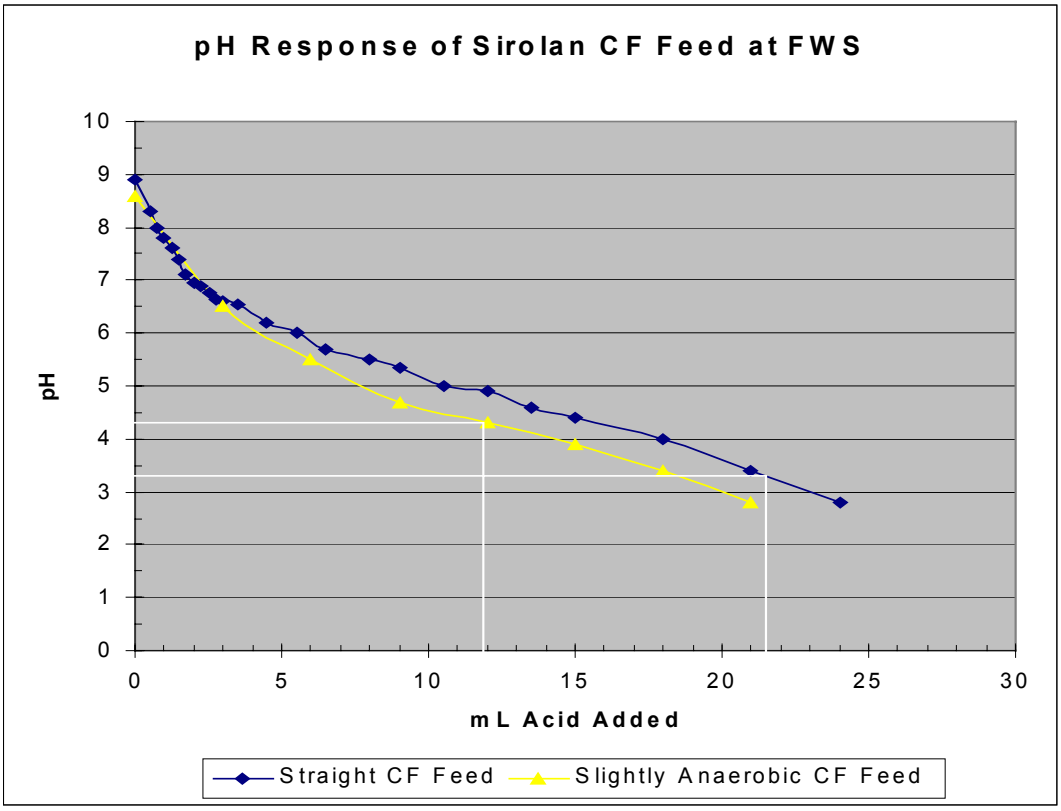


Figure 5.20 Effluent pH response to sulphuric acid addition

From the results of this investigation, not only was the pH at which optimum flocculation occurred increased to pH 4.4, but as shown by Figure 5.20, the quantity of acid required to achieve a given pH adjustment was also reduced in the anaerobic sample. By combination of these two effects it is evident that allowing the heavy flow-down effluent to go even slightly anaerobic can give a saving of up to 45% in acid consumption (the sample tested in this case had only developed an *extremely* mild hydrogen sulphide based 'anaerobic scour liquor' odour, indicating that only a low level of anaerobic activity had been initiated after 14 hours).

Due to the low level of anaerobic activity detected in the second sample, the residence time of 14 hours used here for the anaerobic pre-treatment was judged to be the minimum time necessary for the liquor to develop notable anaerobic growth ***without seeding***. In a continuous flow or fill and draw operation, the required retention time in the anaerobic tanks would be significantly reduced by maintaining a quantity of anaerobic biological culture in

the feed tank at all times. Trials carried out by an English scour where heavy flow-down effluent is held under anaerobic conditions prior to dissolved air flotation treatment have determined the optimum anaerobic retention time for that process to be 12 hours. A German wool scour, which also retains all heavy flow-down effluent under anaerobic conditions prior to dewatering in a decanter centrifuge (without chemical addition), uses a 5-day anaerobic retention time. In the latter example the solid-liquid phase fed to the decanter is drawn from the bottom of the unstirred anaerobic tank. A grease rich top phase is drawn off through a floating weir in the top of this anaerobic tank and is passed through wool grease recovery centrifuges, where a large quantity of wool grease is recovered.

5.2.2.3 Commercial Scale Confirmation of Results

Trials carried out at Kaputone Wool Scour in Christchurch, New Zealand, using a full sized Sirolan CF plant fed from a $30m^3$ anaerobic feed tank, yielded a marked increase in effluent quality while approximately halving the acid consumption of the chemical flocculation process. (Table 5.5)

Table 5.5 Results from Kaputone Wool Scour trials

Feed	**Feed Flow** *(L/hr)*	**Centrate SS** *(mg/L)*	**Centrate SE** *(mg/L)*	**Acid use** *(L/hr)*
Raw Heavy Flow-down	*6,100*	*2,284*	*1,559*	*20*
Raw Heavy Flow-down	*6,500*	*3,350*	*1,376*	*22*
Anaerobic Heavy Flow-down	***6,000***	***265***	***210***	***10***
Anaerobic Heavy Flow-down	***6,000***	***585***	***658***	***11***

5.2.3 DISCUSSION

The results of the analysis carried out into pre-treatment of Sirolan CF feed by anaerobic bio-flocculation indicated that by allowing the effluent to develop anaerobic growth prior to chemical flocculation, a significant improvement in quality of the centrate could be achieved. Consistent with observations made by McLaughlin and Leonard (McLaughlin *et al.* 1992), the effluent that had been treated anaerobically, with subsequent removal of insoluble iron sulphide with the sludge phase, was of much lighter colour than effluent passed directly through the Sirolan CF process.

Alongside this improvement in centrate quality was a concomitant reduction in the acid dosing rate and therefore in the operating cost of the process. For an average 3m operating width New Zealand scour operating the Sirolan CF process, the payback of installing a 12hr holding tank for anaerobic pre-treatment is approximately 10 months (Calculated from 45% reduced acid use at a sulphuric acid cost of $\$0.80L^{-1}$ - Orica Chemnet, May 2002). Furthermore, Charles *et al* (Charles *et al.* 1996) have verified that the destabilisation of the effluent emulsion is due to microbial attack on the nonylphenol-ethoxylate detergent resulting in shortening of the hydrophilic ethoxylate chain. As this process has no effect on the grease phase other than to destabilise and flocculate it, the potential remains to recover this destabilised grease from the surface of the anaerobic reactor. If 50% of residual wool grease in the effluent could be recovered in this way, then the economic impact could be in excess of $3,000 per day worth of saleable wool grease for an average sized New Zealand wool scour (2002 wool grease price at $2.8/kg). Further commercial investigation is planned to quantify and evaluate economic feasibility of integrating the anaerobic bio-flocculation system into the wool scour's existing wool grease recovery plant.

Installing sufficient holding volume to store raw scour effluent for at least 12 hours before chemical flocculation is particularly recommended for all processes where a Sirolan CF system is used to feed an aerobic activated sludge process (such as Sirolan CF-B). The reduced acidity of the centrate from the Sirolan CF process will significantly reduce problems associated with high strength, low pH feed to the aerobic reactor and improve the overall stability of the process. The anaerobic hydraulic retention time of 12 hours is believed to be the minimum period required for reliable bio-flocculation. Charles *et al* (Charles *et al.* 1996) showed a strong relationship ($r^2 = 0.77$ for a sample size of 4) between the level of grease flocculation achieved in the anaerobic treatment and the free surfactant concentration of the raw effluent. In the one sample with negligible free surfactant (but high total surfactant) they showed a significant proportion of wool grease flocculation occurring in the first day, whereas at higher free surfactant concentrations the same level of grease flocculation took up to five days to achieve.

Mercz and Cord-Rudwisch (Mercz *et al.* 1997) found however that, when combined with cationic polymer addition (Zetag 92 with no pH adjustment) a continuous anaerobic treatment with 1-2 day hydraulic retention time was sufficient to give 90% wool grease removal. Longer anaerobic retention times gave better flocculation in the anaerobic stage, but were reported to give no improvement in overall bio-chemical flocculation efficiency. They concluded that there was little relationship between residence time in the anaerobic reactor and overall wool grease removal, and went on to speculate that a 24 hour anaerobic residence

time should be sufficient for optimum total wool grease removal. This work and others (Lapsirikul *et al.* 1994c) also reported that bioflocculation efficiency increased when the anaerobic reactor was left unmixed, something that would require the use of a steep hopper-bottomed tank due to the tendency of the heavy solids in raw scour effluent to settle into a dense mass resembling concrete.

A factor observed in the full-scale tests combining the Sirolan CF process with anaerobic bioflocculation that has not been reported by other researchers was the effectiveness of treating half the heavy flow-down effluent anaerobically, then combining it with the remainder of the raw flow-down before treatment by chemical flocculation. In tests carried out at commercial scale, the chemical flocculation treatment of an effluent consisting of 50% anaerobically treated heavy flow-down effluent combined with 50% raw heavy flow-down effluent gave a similar quality of centrate as reported for effluent that had been 100% treated by anaerobic bioflocculation (Table 5.5). In the instance where the mixed anaerobic / raw feed effluent was used in the Sirolan CF process, the reduced acid requirement typical of anaerobically treated effluent was not observed. Subsequently, although adopting this mode of operation on a commercial scale may significantly reduce the capital cost of a bioflocculation tank due to the requirement that only *half* the heavy flow down effluent need be stored anaerobically for 12 hours, the long-term economic benefits would be less than if a pre-treatment system with capacity to process the entire effluent flow was installed.

The 45% reduction of acid use observed with anaerobically pre-treated effluents also corresponded to a similar reduction in the overall sulphate content of the final effluent discharge. This is due to the fact that approximately 95% of sulphate in the effluent is directly attributable to sulphuric acid addition during chemical flocculation. The other situation therefore where anaerobic pre-treatment may be of significant advantage is where the sulphate content of the final effluent must be reduced. This is particularly relevant to sites where the effluent is discharged to pumped concrete sewers as are used in flat urban areas such as Christchurch and Melbourne. In these cases, high sulphate concentration effluents are corrosive to the sewer pipes, as the sulphate eats away the inter-granular material of the concrete from which the pipes are constructed.

5.3 TURBIDITY CONTROL OF SIROLAN CF

The effluent produced by the Sirolan CF process is often of extremely variable quality. If the type of wool being washed, the amount of water being used in the scour or any number of other parameters are changed, the optimum pH at which the Sirolan CF process should be run also changes. If no action is taken to alter the pH set point of the Sirolan CF process, then effluent is produced with unacceptably high levels of residual suspended solids, wool grease, BOD_5, and COD. If this poorly treated effluent goes unnoticed and is discharged from the site, serious fines for breach of discharge consent may be incurred. Potentially worse still, if the sub-standard effluent is fed to an on-site biological treatment process it may result in catastrophic failure of the biological process requiring a restart that may take several weeks. In one case during this investigation, substrate overloading due to this phenomenon resulted in death of the downstream biological process, requiring approximately eight days to bring the biological reactor system back into full capacity operation.

The most significant advance made in improving the reliability and robustness of operation of the Sirolan CF process proved to be a turbidity monitoring and control system. This process used an optical beam sensor to measure the optical absorbance (proportional to suspended solids and colour) of the centrate. As turbidity sensors are sensitive to interference by air bubbles, the sensor was installed in a bleed line from a de-aeration hopper installed on the feed from the centrifuge into the Sirolan CF-B feed storage tank.

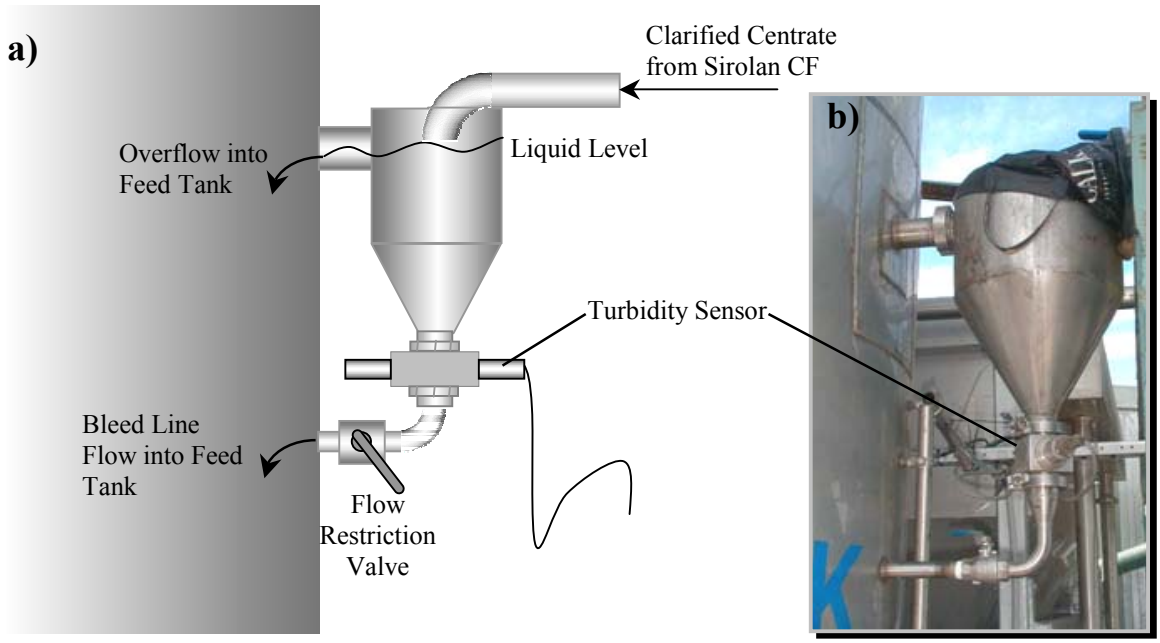


Figure 5.21 a) Turbidity sensor set-up, b) Installed on 50,000L trial plant

Initial investigations into the use of this technology for monitoring the centrate quality showed great potential. Figure 5.22 shows the results of a trial carried out into the suitability of using turbidity as a means of automatically monitoring the quality of effluent produced by the Sirolan CF process. The Sirolan CF process only operates effectively if the effluent to which the polymer flocculent is added is maintained within a precise pH range. This range is generally no more than ±0.4pH of the optimum operating point (which must be determined on a day to day basis). In the trial, the quality of the centrate passed through the turbidity probe was varied by altering the operating pH (and therefore the suspended solids removal efficiency) of the Sirolan CF process. Whether or not the centrate was of acceptable quality to be fed to the biological treatment process was judged by eye (as was only the previously available test method) and this determined the 'acceptable operating zone' as given in Figure 5.22.

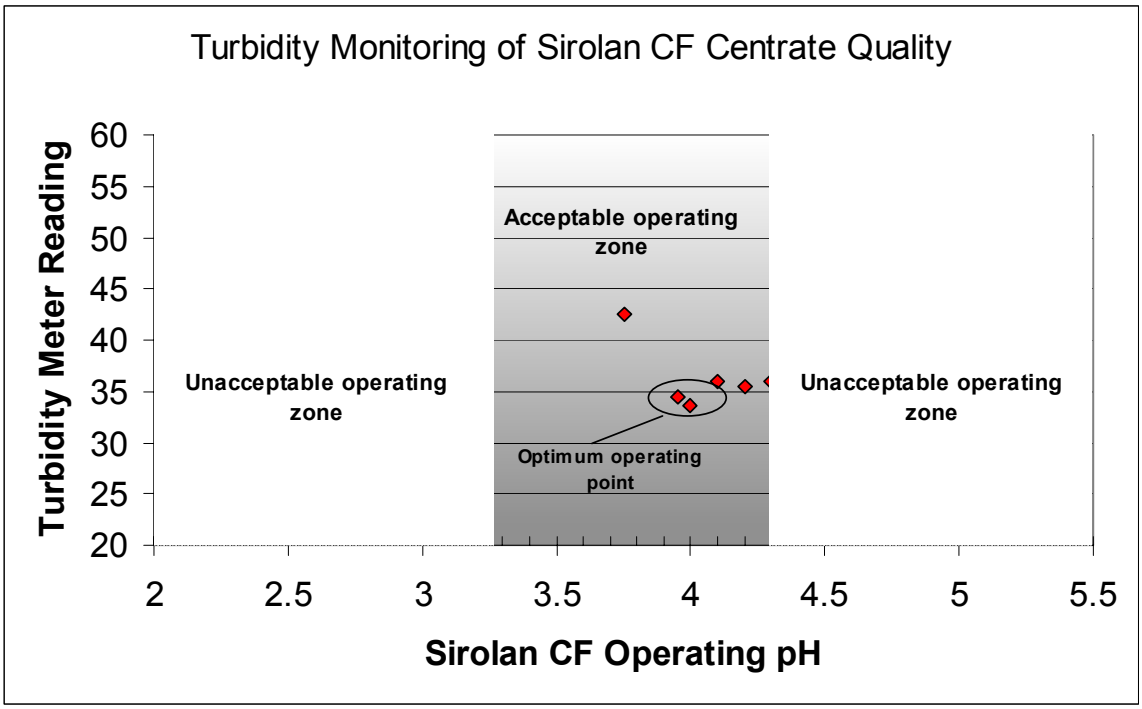


Figure 5.22 Turbidity monitoring of Sirolan CF centrate quality

As can be seen from Figure 5.22, the turbidity meter clearly showed an optimum pH operating point for the Sirolan CF process. This point coincided precisely with the point at which the effluent was subjectively observed to be of optimum optical clarity. This test proved to be repeatable with the turbidity probe easily detecting small changes in the optimum pH at which the Sirolan CF process should be operating. The turbidity – pH curve illustrated in Figure 5.22 moved relative to both the pH and turbidity axis day by day due to wool type, scour operational parameters, and turbidity probe fouling but the characteristic bell

shape curve with a clear optimum operating point was maintained under all operational conditions encountered.

The asymmetry of the bell shaped curve about the optimum operating point was attributed to fine bubbles being generated in the effluent solution in the presence of excess acid. This resulted in the measured turbidity increasing more rapidly below the optimum operating point than above. For this reason, the level of turbidity that resulted in an 'acceptable looking' feed for the biological reactor was higher at low pH than at higher pH.

The tendency of the turbidity probe to consistently detect an optimum pH for the operation of the Sirolan CF pre-treatment process raised the option of using this device to detect and automatically set the optimum operating pH of the process. Due to the optimum operating point being a local minima, with both an increase and a decrease in operating pH leading to a decrease in product quality, a PLC (Process Logic Controller) was required to run the control loop as opposed to a simple and inexpensive PID (Proportional / Integral / Derivative) controller.

The control strategy chosen was to use a simple search algorithm to determine the pH at which the minimum turbidity occurred, and then pass this on to the PID pH control loop as the new pH operating set-point. The benefits of this system over the previous system for selection of the pH set point were:

- Subjectivity of operator removed from the control loop
- Process becomes less dependent on operator supervision
- Turbidity probe fouling has limited effect on effectiveness of the control loop
- Automatic compensation for pH probe drift, maintaining optimum product quality at all times

Three alarms were built into the turbidity monitoring and control system:

1. Trigger Search – If the currently measured turbidity of the centrate increases by more than a user-entered margin above the current optimum turbidity, a search algorithm is triggered to determine a new optimum operating pH.

2. User Alarm – If the turbidity rises above a user-entered maximum permissible value, then an audible alarm is sounded. This can mean that the control loop has failed or the sensor head of the turbidity probe needs cleaning.

3. System Fail – If the turbidity continues to rise above the level at which the user alarm is sounded, then the process will either be automatically shut down or the product effluent will be diverted to an off-spec tank for reprocessing before it is allowed to enter the biological treatment system.

This system proved extremely effective in controlling the pilot plant Sirolan CF process and ensuring that the effluent passed on to biological treatment was pre-treated to the highest possible level at all times. As the turbidity probe quantified the actual quality of the product effluent, it detected any problem that occurred with the pre-treatment process. This proved to be an invaluable asset when operating the process on a continuous basis, as the one parameter could be used to detect problems with any component of the effluent feed, pH and flocculent dosing systems or decanter centrifuge, and shut the process down if the problem could not be remedied automatically. This automated intervention prevented raw wool scour effluent from ever being fed to the biological treatment system, thus enabling the pre-treatment system to be operated unattended for extended periods of time.

Installation of this system with new Sirolan CF processes has proven extremely successful with the resultant effluent treatment system requiring a minimum of operator supervision, and optimum efficiency of the treatment process being maintained at all times.

Commercial scours that had purchased and implemented this technology at the time of publishing were:

- EP Robinson Ltd, Australia
- Tavares Scouring, Portugal
- Kaputone Wool Scour, New Zealand
- Ashburton Wool Scour, New Zealand

6 AEROBIC ACTIVATED SLUDGE SYSTEM. LABORATORY SCALE STUDIES.

6.1 INTRODUCTION

After being treated by the Sirolan CF process, the clarified effluent is to be further processed by an activated sludge system for removal of residual biodegradable compounds. In addition to the qualities of this effluent stream listed as "Sirolan CF Centrate" in Table 5.2, the effluent to be fed to the biological treatment system typically contains the following components:

Table 6.1 Nutrient concentrations in Sirolan CF centrate

Compound	Concentration [mg/L]
Soluble Sulphate	9,000 - 12,000
Ammonia Nitrogen	100 - 500
Organic Nitrogen	300
Nitrate Nitrogen	5 - 20
Dissolved Reactive Phosphorus	50
Potassium	1000 - 6000

Virtually all activated sludge processes consist of the main components shown in Figure 6.1 on the following page. The feed substrate (In this case Sirolan CF centrate) is fed to the large aerated vessel (1) containing a concentrated suspended culture of aerobic micro-organisms. The effluent is held in this tank for a period of time determined by the rate at which the degradable compounds are metabolised by the microbial culture. Typical hydraulic residence times in the aeration vessel range from 3 – 12 hours for domestic sewerage treatment to more than 5 days for some systems processing concentrated industrial effluents (Eckenfelder 1992).

The bio-chemical reaction occurring in the aeration vessel can be simplified to:

$$\text{Biodegradable Pollutants} + \text{Oxygen} \xrightarrow{\text{Microbial cells}} \text{Carbon Dioxide} + \text{Water} + \text{More Cells} \qquad (16)$$

in which the cells (or *Biomass*) are analogous to a heterogeneous catalyst, with the additional benefit that more catalyst is produced as a reaction product.

In the next stage of the process, the mixed liquor from the aeration vessel is fed to a solids separation system (2), typically a gravity clarifier, where the microbial culture is settled out

and recycled to the aeration vessel where it is used to degrade fresh feed again. The supernatant (liquid overflow) of the clarifier is discharged to drain or sent to further treatment such as evaporation.

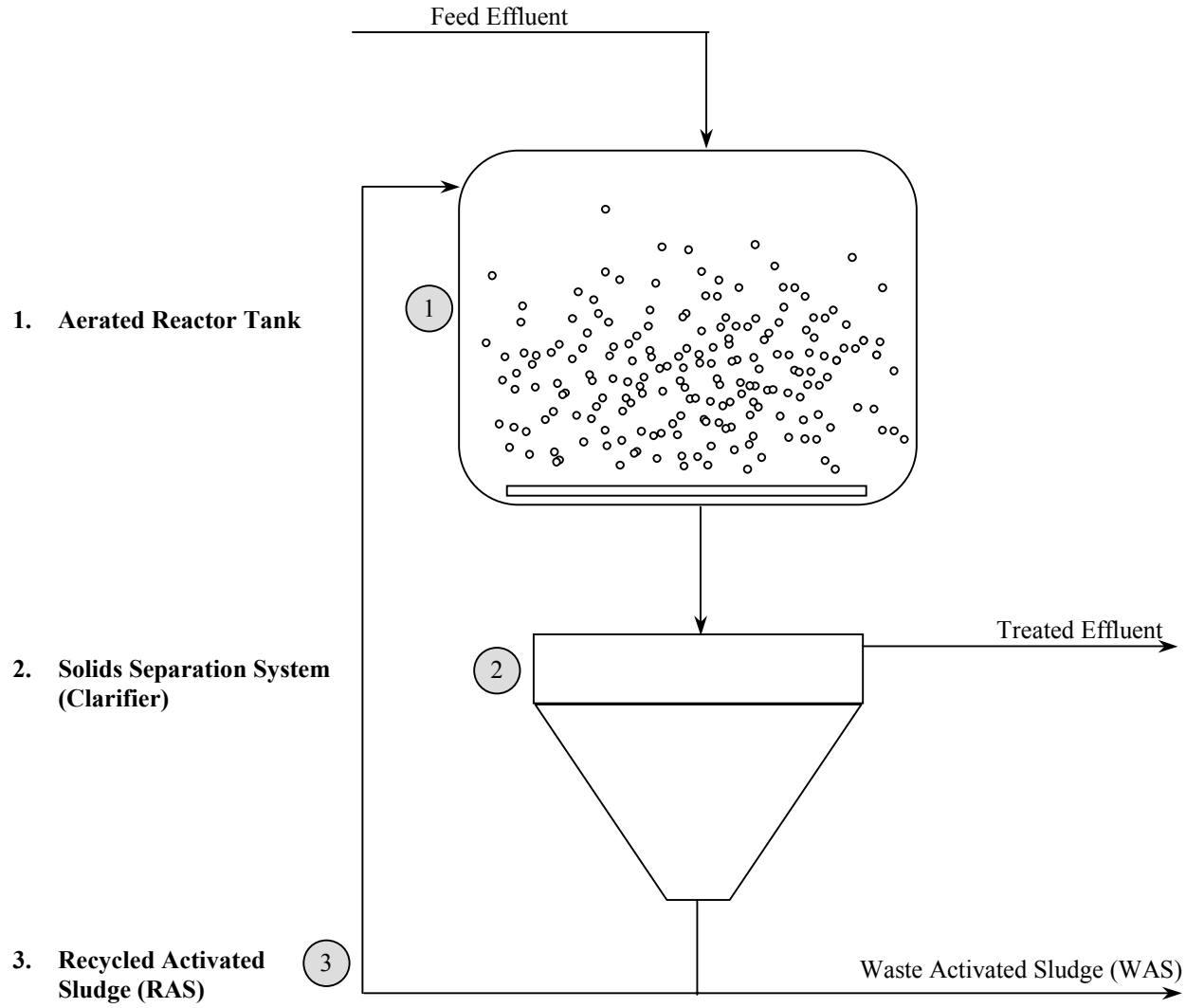


Figure 6.1 Typical activated sludge system

Depending primarily on the feed effluent characteristics, a continuous mix activated sludge process (Figure 6.1), a plug flow activated sludge system (Figure 6.2), or sequencing batch reactor (Figure 6.3) may be used.

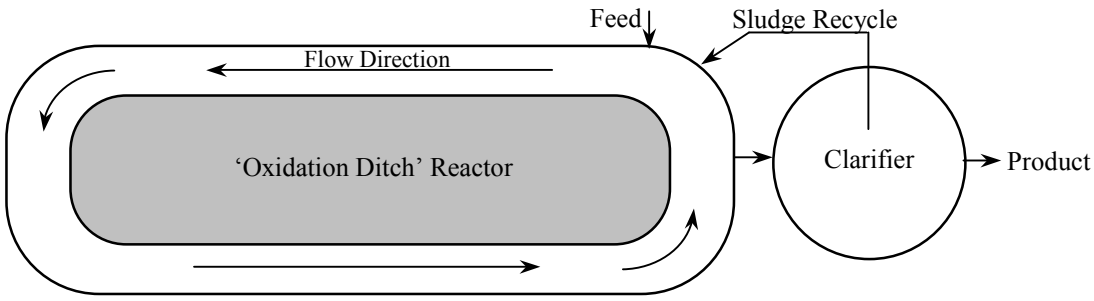


Figure 6.2 'Oxidation Ditch' plug flow reactor

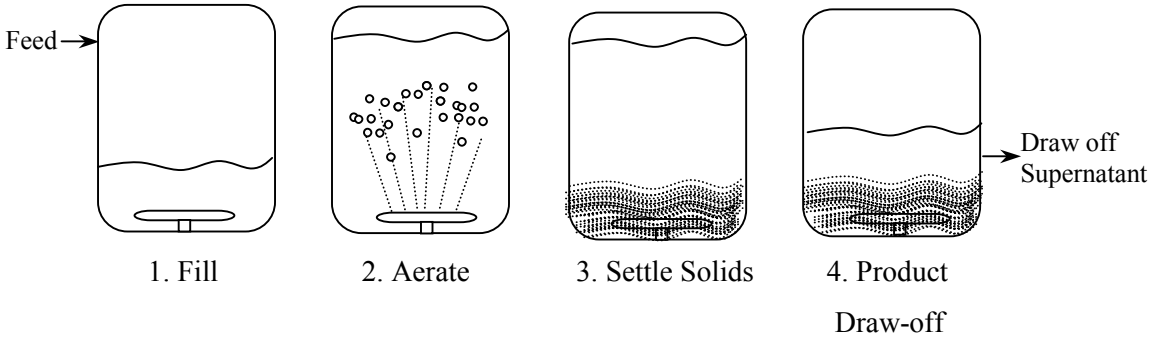


Figure 6.3 Sequencing batch reactor

A plug flow reactor is most commonly used when treating readily degradable effluent, which is susceptible to filamentous bulking. By feeding concentrated substrate at one point in the loop a concentration gradient is introduced between the feed and product draw-off points. This provides a low substrate concentration in the product stream, without requiring the entire reactor to operate at this low concentration, which would favour the growth of undesirable filamentous bacteria that have poor gravity settling characteristics (Daigger *et al.* 1992).

Sequencing Batch Reactors (SBRs), also known as 'fill and draw' systems are not commonly used for traditional activated sludge purposes, but are commonly used in systems where biological nutrient removal is required. This is due to the ease with which anoxic, anaerobic and aerobic conditions can all be achieved in the one vessel simply by turning the aeration system on and off strategically during the batch process.

6.1.1 BIOLOGICAL KINETICS

Biological reactions, as simplified by Equation (16), take place by a process where substrate is taken up by living cells and is subsequently metabolised by enzymatic reactions within the cells. The actual reaction sequence responsible for energy generation in aerobic (oxygen consuming) cells is somewhat more complex. This is summarised in Figure 6.4.

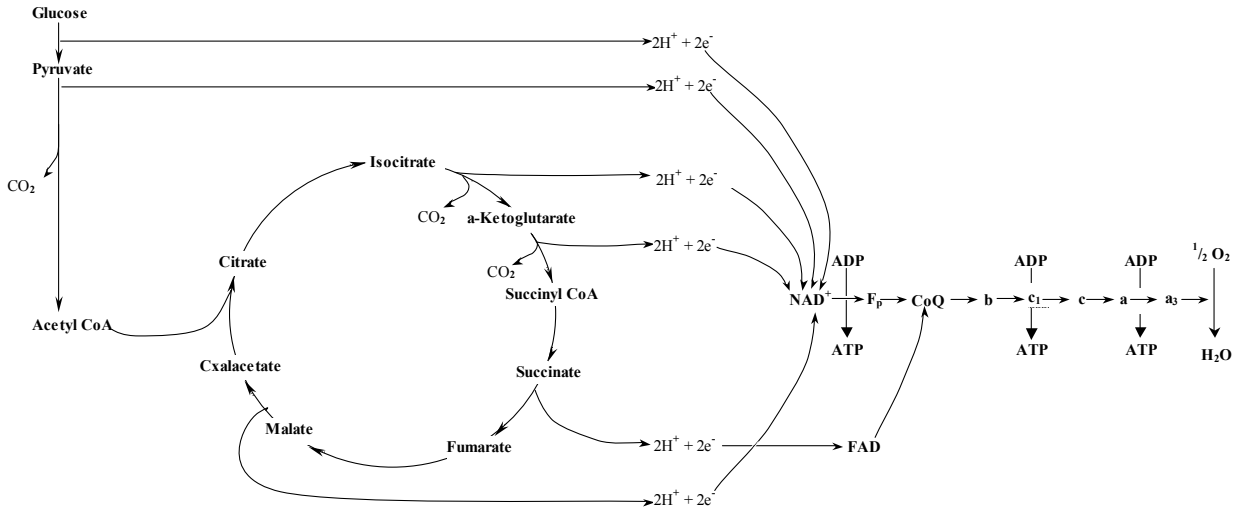


Figure 6.4 TCA cycle for energy production in aerobic cells

This process produces up to 38 units of ATP (ATP, or Adenosine-triphosphate is the energy supply media used to power cellular processes such as growth and reproduction) from each unit of glucose substrate that enters the cycle. The other main products of the process are CO_2 and H_2O. Alternatively, in anaerobic processes which do not use oxygen as a terminal electron acceptor (as occurs in the right hand side of the electron transport chain in Figure 6.4) only the glucose → pyruvate stage of the TCA cycle is applied (top left corner of Figure 6.4) with the much lower energy production rate of 2 units of ATP produced per unit of glucose consumed (Garrett *et al.* 1995). This difference illustrates the much higher efficiency of aerobic over anaerobic biological processes. The activated sludge process is an aerobic biological system that includes a solids separation process for recycling the live biomass (activated sludge) from the settling system back to the reactor vessel (as shown in Figure 6.1). The concentration of micro-organisms available in the reactor vessel to digest the incoming waste is therefore maximised, thus increasing the overall rate of contaminant removal. The effectiveness of this can be illustrated by carrying out a mass balance for the substrate (pollution loading) in the continuous mix aeration vessel.

$$\overbrace{V\frac{dS}{dt}=0}^{\text{At Steady State}}=\underbrace{QS_1-QS}_{\substack{\text{Substrate in –}\\ \text{Substrate out}}}-\overbrace{V\left(\frac{\mu}{Y_h}X\right)}^{\substack{\text{Biological Consumption}\\ \text{of Substrate}}} \qquad (17)$$

where for most readily degradable substrates:

$$\mu=\frac{\hat{\mu}S}{(K_s+S)} \qquad (18)$$

and:

V	=	Volume of the reactor vessel [m^3]
S_1	=	Substrate concentration in the feed [g/m^3]
S	=	Substrate concentration in the treated effluent [g/m^3]
t	=	Time [hr]
Q	=	Volumetric flow rate [m^3/hr]
Y_h	=	Biomass yield coefficient $g_{MLSS}/g_{Substrate}$
X	=	Biomass concentration in reactor [g/m^3]
$\hat{\mu}$	=	Monod maximum biomass growth rate [hr^{-1}]
K_s	=	Monod rate coefficient [g/m^3]

By rearranging (17) we can show that the level of substrate removal $Q(S_1 – S)$ achieved is directly proportional to the quantity of viable micro-organisms in the reactor (X):

$$Q(S_1-S)=V\left(\frac{\mu}{Y_h}X\right) \qquad (19)$$

As the goal of the process is to optimise this substrate removal, the inclusion of a selective recycle loop that accumulates biomass (X) in the reactor vessel is extremely favourable.

Equation (18) is known as the Monod equation. This is an empirical cell growth model similar in form to the Michaelis-Menten equation for enzyme kinetic theory. The Monod

equation is applicable to many simple biological systems where substrate removal is achieved by growing micro-organisms. Comparison of this with the structure of the Michalis-Menten relationship for enzyme velocity (or reaction rate) given in Equation (20) suggests the possibility that biological reactions that follow Monod kinetics may be controlled by enzyme kinetics.

$$V_0 = \frac{V_{\max}[S]}{(K_s + [S])} \qquad (20)$$

V_0 = Initial enzyme velocity
V_{max} = Maximum attainable enzyme velocity
[S] = Substrate concentration
K_S = Disassociation constant of enzyme-substrate complex

This relationship is based on the assumption that it is the disassociation of the enzyme – substrate complex that is the rate-limiting step of the enzymatic reaction and has become the fundamental basis of most enzyme kinetics to date (Keleti 1986). Bearing in mind that the adsorption-desorption processes between the substrate and enzyme are the dominating kinetic factor in the rate of the enzymatic reaction, it can be seen that the Michalis-Menten model is functionally similar to the Langmuir isotherm model for adsorption of material onto the surface of a heterogeneous catalyst (Equation 21).

$$a = \frac{a_\infty P}{(\frac{1}{b} + P)} \qquad (21)$$

a = Relative quantity of adsorbed substrate
a_∞ = Maximum amount of substrate that can be adsorbed
P = Pressure
b = Constant (characteristic of the adsorbed material)

One case where the straight Monod model does not adequately represent the reaction kinetics observed in a bio-chemical system is where a high concentration of the substrate is toxic or inhibitory to the growth of the micro-organisms. Equation (18) shows that as the concentration of substrate in a Monod type system increases (S in a completely mixed reactor), so does the specific cellular growth rate of the micro-organisms (μ).

In the Haldane equation, which describes the specific growth rate of the micro-organisms under substrate inhibition kinetics, the term K_{IS} (the coefficient of substrate inhibition) is included. Under these conditions the specific growth rate is given as:

$$\mu_{IS} = \frac{\hat{\mu} S}{(K_s + S + \frac{S^2}{K_{IS}})} \qquad (22)$$

μ_{IS} is then used in Equation (17) in place of μ. Figure 6.5 shows a comparison of the growth rate predicted by the two equations. In the case where S « K_{IS}, equation (22) tends towards Equation (19) and the growth rate predicted is the same. At higher substrate concentrations, where the toxicity of the substrate begins to take effect the two systems behave very differently.

This relationship is also derived from enzyme kinetic theory. This time the modification of the Monod model for substrate inhibition corresponds to Haldane's enzymatic relationship for substrate-excess inhibition (Haldane 1930):

$$V_0 = \frac{V_{max}[S]}{(K_s + [S] + \frac{[S]^2}{K_{IS}})} \qquad (23)$$

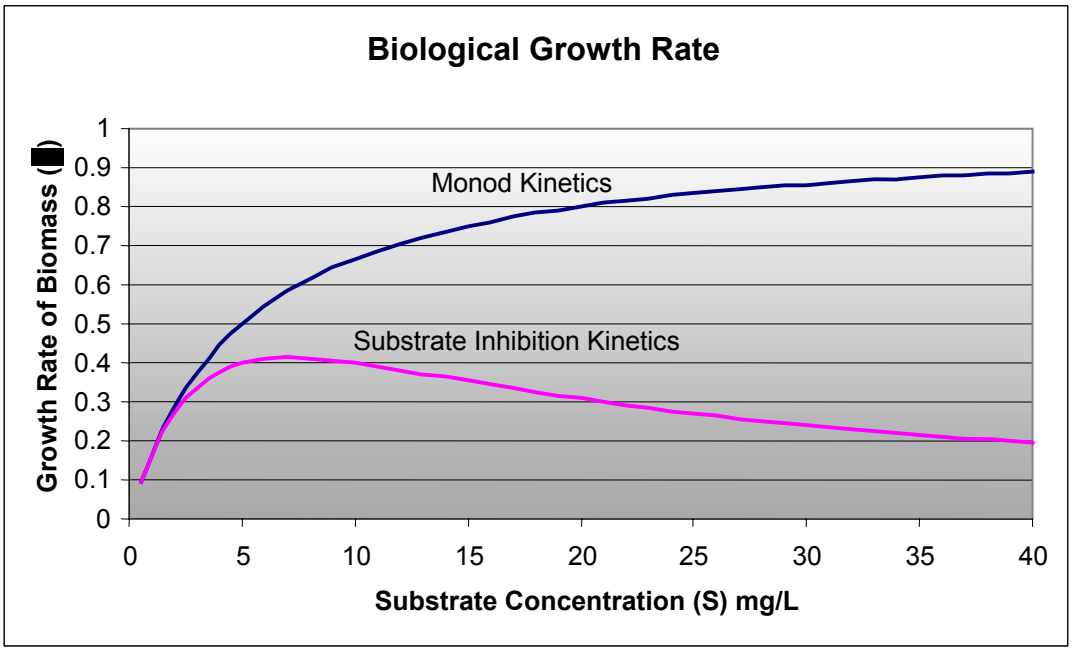


Figure 6.5 Comparison of Monod and inhibition kinetics: $\mu = 1$, $K_S = 5$, $K_{IS} = 10$

Although the model attributed to Haldane, as illustrated by Equation (22), was the first to be developed to model this type of substrate – growth-rate interaction, the wide range of substrates and microbial species used in industrial applications has led to a plethora of similar kinetic models being developed to represent their interactions. Not all of these have such strong theoretical backgrounds as the Haldane model and many are purely empirical.

Under the category of 'Substrate Inhibition' alone, Orhon (Orhon *et al.* 1994) gives the following examples of kinetic models that have been developed over the last 40 years:

$$\mu_{IS} = \frac{\hat{\mu}\, S}{(K_s + S)(1 + \frac{S}{K_{IS}})} \qquad (24)$$

$$\mu_{IS} = \frac{\hat{\mu}\, S(1 + \frac{S}{K_S})}{(K_s + S + \frac{S^2}{K_{IS}})} \qquad (25)$$

$$\mu_{IS} = \frac{\hat{\mu}\, S}{K_s + S + (\frac{S^2}{K_{IS}})(1 + \frac{S}{K})} \qquad (26)$$

$$\mu_{IS} = \frac{\hat{\mu} S}{K_s + S} e^{-S/K_{IS}} \qquad (27)$$

$$\mu_{IS} = \hat{\mu}(e^{-S/K_{IS}} - e^{-S/K_S}) \qquad (28)$$

$$\left.\begin{aligned} \mu_{IS} &= \frac{\hat{\mu}\, S}{K_s + S} \quad when \quad S < S^* \\ \mu_{IS} &= \frac{\hat{\mu}\, S}{K_s + S} - K_{IS}(S - S^*) \quad when \quad S > S^* \end{aligned}\right\} \qquad (29)$$

Mulchandani and Luong (Mulchandani *et al.* 1989) presented a critical review of these models, which reported that Equation (24), originally proposed by Haldane (Haldane 1930), accurately modelled the response of a wide range of micro-organisms to inhibitory substrates under both batch and continuous culture conditions. Equations (25) - (27) developed by

Edwards (Edwards 1970) were shown to give little improvement over Haldane's original model despite the inclusion of an extra parameter. Based on a diffusion-controlled substrate supply Edwards further developed Equation (28) which again proved nearly equal in performance to Equation (24). Despite the discontinuity introduced at S^*, the system illustrated by Equation (29) accounts well for the lack of inhibition below a certain critical substrate concentration (S^*) followed by a linear decrease in growth rate above this critical substrate concentration. Unlike the Haldane based models this last one developed by Wayman and Tseng (Wayman *et al.* 1976) also accounts for the existence of a maximum substrate concentration above which the micro-organisms will be completely inhibited with a growth rate of zero.

The third type of kinetic model relevant to this investigation is based on a pseudo toxic concentration model for pH inhibition. Ko (Ko *et al.* 2001) studied a range of kinetic models applicable to activated sludge systems operating in acidic or basic environments. In this work a number of proposed kinetic models were evaluated under a wide range of pH conditions. The most flexible and reliable model proved to be one developed by (Choi 1999) in which pH is expressed as a pseudo toxic concentration (C_{PT})

$$C_{PT} = \left(pH_{th} - pH_r\right)^2 \qquad (30)$$

where pH_{th} is the pH where inhibition begins to take place (~6.5 for most acidic activated sludge systems).

pH_r is the pH of the reactor.

This model was confirmed by Ko to be reliable over a wide range of nitrifying and less acidophilic activated sludge bacteria (Ko *et al.* 2001)

In this model, the pseudo toxic concentration is used to modify the maximum growth rate coefficient of the standard kinetic models as illustrated by Equation (31). This is consistent with the approach taken by non-competitive enzyme inhibition kinetics upon which the model is based (Keleti 1986).

$$\hat{\mu}_I = \frac{\hat{\mu}}{(1 + \frac{C_{PT}}{K_I})} \qquad (31)$$

where:

$\hat{\mu}$ = Maximum biomass growth rate (without inhibition)

$\hat{\mu}_I$ = Maximum biomass growth rate adjusted for non-competitive inhibition

K_I = Non-competitive inhibition rate coefficient

C_{PT} = Pseudo toxic concentration

K_I can then be determined by the Lineweaver – Burke plot of $\frac{\hat{\mu}}{\hat{\mu}_I}$ against C_{PT} for basic and acidic conditions respectively.

From Equation (31) it can be seen that:

$$\frac{\hat{\mu}}{\hat{\mu}_I} = \frac{K_I + C_{PT}}{K_I} = 1 + \frac{C_{PT}}{K_I} \qquad (32)$$

$\frac{\hat{\mu}}{\hat{\mu}_I}$ can be determined by respirometry, and if the pH does follow non-competitive inhibition kinetics the subsequent plot of $\frac{\hat{\mu}}{\hat{\mu}_I}$ against C_{PT} will prove linear with a y-intercept of 1, and a slope of $\frac{1}{K_I}$.

By combining these key kinetic models as appropriate, the growth rate (and therefore substrate uptake rate) of the biological system can be modelled. This can be a very useful tool for designing and optimising biological treatment systems.

6.1.2 REACTOR SELECTION

Among other more case specific parameters, the ideal type of reactor for a given treatment process depends on the substrate characteristics, the type of reaction kinetics the biological reaction follows, and space available, as well as capital and operating cost considerations.

For a first order reaction where the reaction rate is directly proportional to the substrate concentration, the most economical solution is often a plug flow reactor (such as the oxidation ditch in Figure 6.2) or a set of small complete mix reactors operating in series, which can be used to mimic a plug flow regime. For the latter option, duplication of aeration and mixing equipment often limits the process to two or three reactors in series. Figure 6.6 illustrates how concentration profiles (and therefore reaction rate) vary between the reactor configurations given.

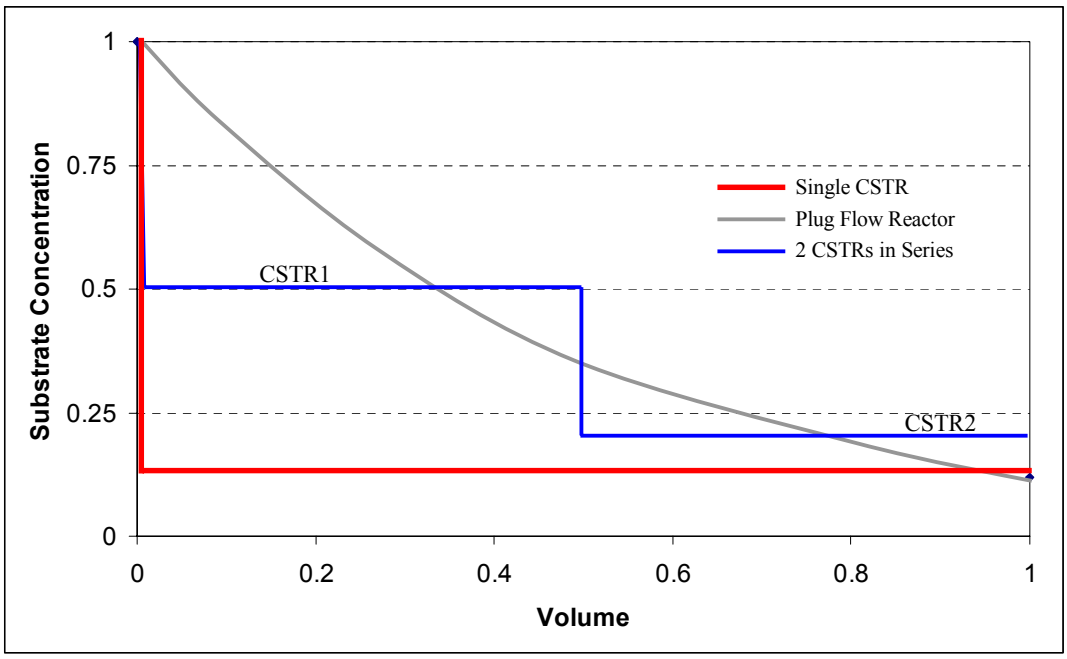


Figure 6.6 First order reaction kinetics

Furthermore, taking the simple case of first order kinetics where substrate uptake rate (r_s) is directly proportional to substrate concentration, we can perform a steady-state mass balance over continuous mix (CSTR) and plug flow reactors to determine the reactor size required to achieve a given conversion of feed substrate to product:

$$V\frac{dS}{dt} = 0 = (QS_1 - QS) = r_S V \qquad (33)$$

and by introducing the Conversion Ratio (Z):

$$Z = \frac{QS_1 - QS}{QS_1} \quad \therefore \quad (QS_1 - QS) = ZQS_1 \qquad (34)$$

we can obtain the relationship:

$$\frac{V}{QS_1} = \frac{Z}{-r_S} \qquad (35)$$

Likewise, from the mass balance over a plug flow reactor:

$$\frac{d(QS)}{d(V)} = r_s \qquad (36)$$

so from the definition of conversion ratio (Z) above:

$$\frac{QS_1\, d(Z)}{d(V)} = -r_s \qquad (37)$$

and integrating we get:

$$\int_1^V \frac{1}{QS_1} dV = \int_1^Z \frac{1}{-r_s} dZ \qquad (38)$$

which yields:

$$\frac{V}{QS_1} = \int_1^Z \frac{1}{-r_s} dZ \qquad (39)$$

Therefore if we plot $\frac{1}{-r_s}$ against conversion ratio (Z) we can illustrate the impact of reactor configuration on total volume of reactor required to achieve a given level of substrate conversion.

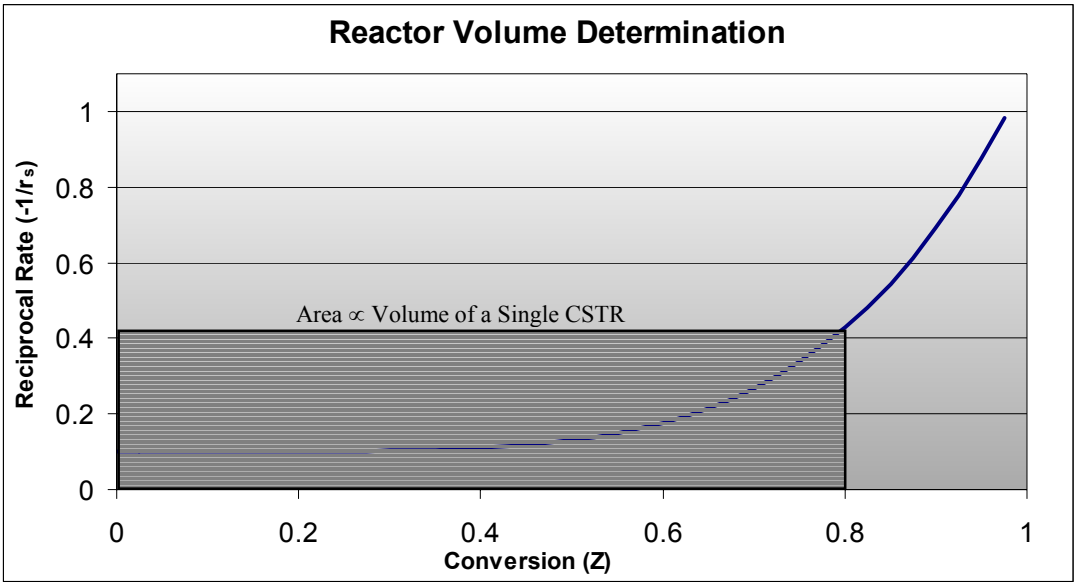


Figure 6.7 Volume required for a single CSTR to achieve 80% conversion

The curve in Figure 6.7 was plotted by using the arbitrarily chosen parameters k = 1hr^{-1}, S_1 = 10 kmol/L in the first order rate equation:

$$-r_s = kS \qquad (40)$$

with Z substituted for S by use of Equation (34).

To achieve a substrate conversion of 80% in a single CSTR reactor it can be seen from Equation (35) that the reactor volume can be determined by the area of the box overlaid on Figure 6.7.

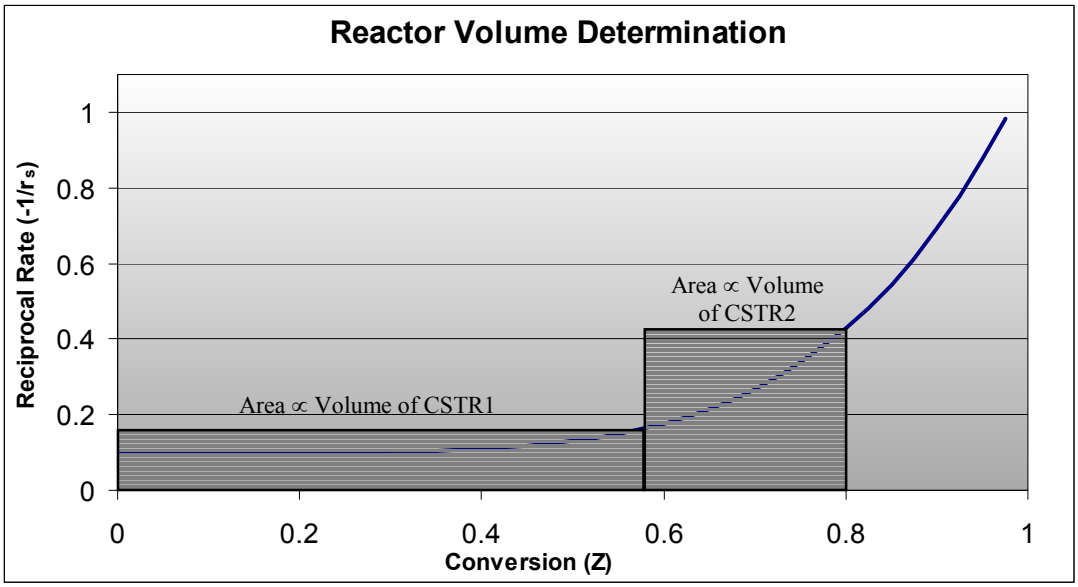


Figure 6.8 Volume required for two CSTRs in series to achieve 80% conversion

For two CSTRs operating in series, the feed to the second CSTR is the product of the first. Therefore in similar manner to the procedure carried out on Figure 6.7, Equation (35) can be used to show that the volume of each reactor is proportional to the respective areas of the two boxes overlaid on Figure 6.8.

Note that for a first order reaction such as this, the combined total volume required to achieve a given conversion is significantly less when operating two reactors in series than when operating one single large CSTR.

By this method, we can show that the most economical solution for this type of reaction may well be to use a plug flow reactor such as the oxidation ditch in Figure 6.2. Equation (39) shows that the volume of plug flow reactor required to achieve a certain conversion is proportional to the integral of (i.e. area under) the $\frac{1}{-r_s}$ vs Z curve itself, and is therefore the minimum theoretical volume in which the reaction can be carried out (Figure 6.9).

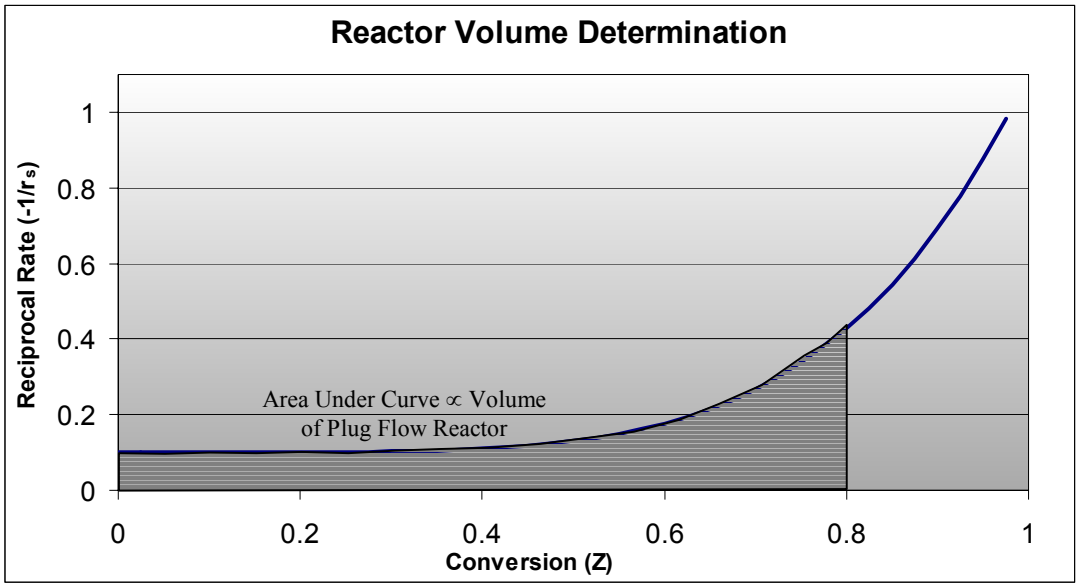


Figure 6.9 Volume required for a plug flow reactor to achieve 80% conversion

Conversely, if the substrate is inhibitory at high concentration as detailed in Section 6.1.1 above, then a larger initial volume, as would be given by one large CSTR (or multiple CSTR's in parallel) would be required to provide sufficient initial dilution of the inhibitory compound(s) that are entering the reactor. Under substrate inhibition kinetics the reactor size must therefore not only be determined based on the level of substrate removal required, but must also give sufficient dilution of incoming substrate to allow the microbial culture to function without suffering toxic effects from the inhibitory compounds in the substrate.

To Illustrate this point, Figure 6.5 can be inverted by using the reciprocal of μ as -1/r, and using equation (34) to convert substrate concentration (S) to conversion (Z):

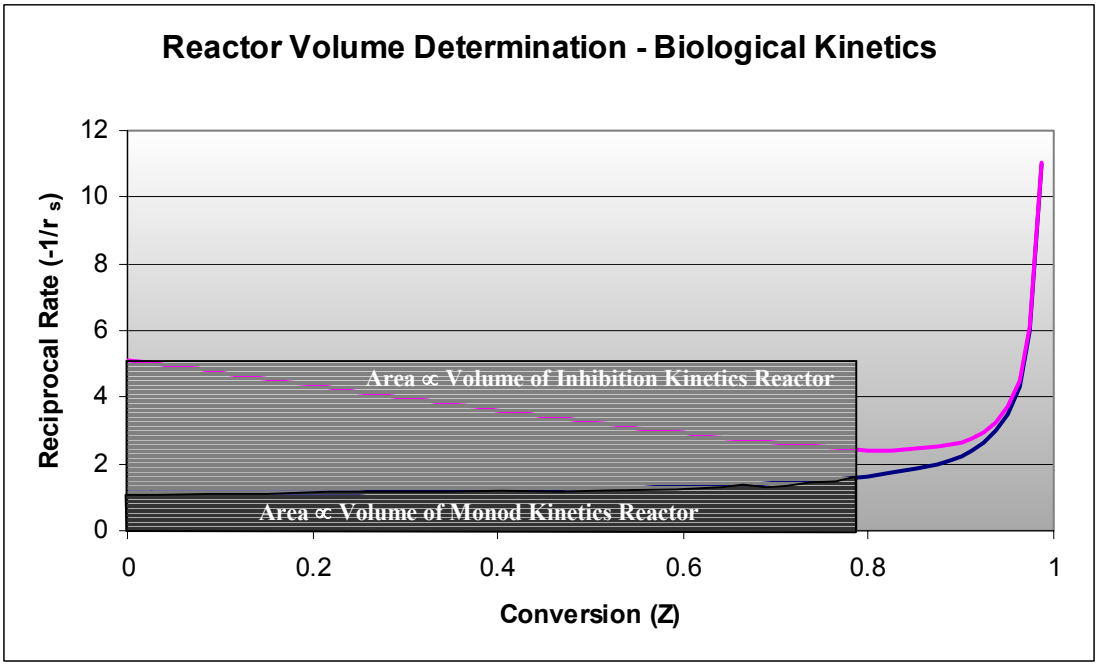


Figure 6.10 Minimum volume required for reactors following biological kinetics to achieve 80% conversion

As Figure 6.10 shows, reactions following Monod style kinetics (the bottom curve in Figure 6.10) display similar rate characteristics to first order reaction kinetics – consequently the use of a plug flow reactor will often be an economical choice. Note also that in Figure 6.10 the volume required to achieve 80% conversion in this particular Monod system would differ little between a plug flow and single CSTR reactor. This is due to the flatness of the reciprocal rate curve below this level of conversion. Alternatively, if 99% conversion were desired the volume of a single CSTR required would be more than twice that of the equivalent plug flow reactor.

In the case of the reactor that is modelled by substrate inhibition kinetics, the reaction rate profile is very different to the profile of a reaction that follows first order kinetics. In this case a large initial volume (as is provided by a single large CSTR) is required to dilute the effluent down to a point where the biological reaction can proceed. This example illustrates that when dealing with systems that contain inhibitory or toxic compounds, the target substrate concentration may be of less importance to the process design than determining what level of inhibitory compound dilution is required to allow stable operation of the process.

Other more process-specific factors also generally influence reactor selection for industrial effluent treatment. These include:

- Prevention of sludge bulking. If a readily degradable effluent (such as sugar refining waste) is treated in a complete mix reactor, problems will often be encountered with filamentous bulking due to low substrate concentration in the reactor. This will often lead to excessive suspended solids in the treated effluent and potential biomass washout with subsequent failure of the reactor.
- Nutrient Removal. If levels of organic nutrients in the treated effluent (particularly nitrogen and phosphorus) must be reduced, then extra anoxic and anaerobic vessels can be combined in series with the main digestion vessel to facilitate removal of these components.
- Equalisation. In sites where either the flow or strength of the feed effluent varies significantly, extra storage volume must be supplied prior to (or in) the main digester to balance out these fluctuations.

6.1.3 THEORY OF SOLIDS SETTLING

Theoretically the solids settling rate of a given particle can be determined from its size, the relative density between the particle and the fluid, and the fluid properties.

The drag force on a particle moving through a liquid can be expressed as:

$$F_d = \frac{CA_p \rho_f u^2}{2} \quad (41)$$

Where: F_d = Drag force [N]

C = Drag coefficient

A_p = Projected area of the particle in the direction of motion [m^2]

ρ_f = Density of the fluid [kg/m^3]

u = Relative velocity between the particle and the liquid [m/s]

g_c = Dimensional constant (e.g. gravity) [m/s^2]

At the terminal velocity (or free settling velocity) where the particle is moving at a constant rate under gravity, the drag force is equal to the gravitational force acting on the particle:

$$F_g = m_p g_c \frac{\rho_p - \rho_f}{\rho_p} = \frac{CA_p \rho_f u^2}{2} \quad (42)$$

Where

F_g = Force due to gravity [N]

ρ_p = Density of the particle [kg/m^3]

m_p = Mass of the particle [kg]

From this expression, the free settling velocity can then be expressed as:

$$u = \sqrt{\frac{2mg_c(\rho_p - \rho_f)}{CA_p \rho_p \rho_f}} \quad (43)$$

Assuming the particles are spherical, the dimensionless drag coefficient 'C' is often given the following values depending on the Reynolds number range:

Table 6.2 Correlation of drag coefficient to particle Reynolds number for spherical particles

	Reynolds No.	Correlation
Laminar Settling	$1x10^{-4} < Re_p < 2.0$	$C = 24/Re_p$
Intermediate Settling	$2.0 < Re_p < 500$	$C = 18.5/Re_p^{0.6}$
Turbulent Settling	$500 < Re_p < 2x10^5$	$C = 0.44$

(Oldshue 1983)

where the dimensionless particle Reynolds number is expressed as:

$$\mathrm{Re}_p = \frac{D_p u \rho_f}{\mu} \qquad (44)$$

and:

D_p = Particle diameter [m]

μ = Fluid viscosity [Pa.s]

As the goal of the procedure is to determine the free settling velocity of the particles suspended in the liquid phase, and the velocity of the particle is also required to determine the Reynolds number, this process becomes an iterative one with the initially calculated velocity used to re-determine the Reynolds number, drag coefficient, and a new more accurate free settling velocity.

Charts are available in the literature (Hottovy *et al.* 1979; Perry *et al.* 1997) for correlation of Reynolds number to drag coefficient for various non-spherical particle shapes.

In an activated sludge system however, where the concentration of solids is typically high and the biological solids used are selected for their ability to form highly flocculated conglomerates, the settling velocity does not remain constant, but increases as the size of the particles grow by contacting and sticking to other particles in the suspension. For a well flocculated activated sludge the bacteria that make up the sludge, despite typically being less than 10μm in individual size (Pelczar *et al.* 1993), can form flocculated macro-particles of as much as 5 – 10mm in diameter.

In the design of processes for the gravity settling of flocculated liquors it is highly recommended that the settling velocity is determined by direct measurement of flocculated solids that have undergone a flocculation – contacting process as similar as possible to that expected in the industrial process. The settling test itself should be carried out in a large graduated cylinder, which is stirred at a speed of 4 to 5 revolutions per hour ensuring that the

liquid velocity is no more than 1cm/s at the periphery of the cylinder (Clesceri *et al.* 1998). This simulates the hydraulic conditions in a full-scale clarifier.

In a high concentration flocculated suspension, zone settling tends to occur. This is where the suspended particles flocculate into similar sized 'flocs', which then settle as a blanket with a distinct interface between the solids and supernatant. As these flocs accumulate in the bottom of the settling vessel, compression thickening of the accumulated solids occurs.

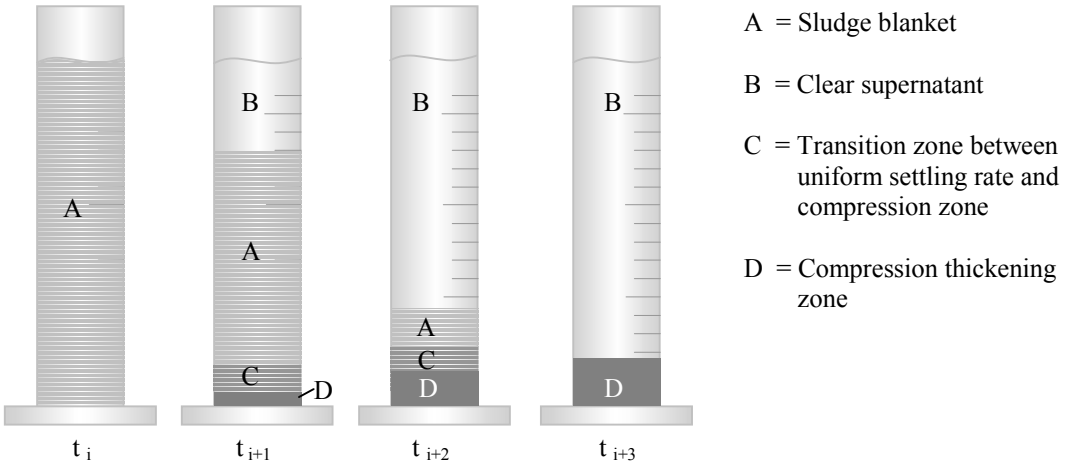


Figure 6.11 Zone settling in a flocculated solids suspension – Adapted from Eckenfelder (Eckenfelder 1989)

The flocculent nature of activated sludge settling has been extensively studied, as a failure to form effectively settling sludge is one of the leading reasons for failure of activated sludge treatment plants (Eikelboom 1974; Steiner *et al.* 1976). The leading causes of poor sludge settling are filamentous bulking – a proliferation of filamentous bacteria which do not settle out of the solution, and the growth of pin-point flocs, which do not flocculate together into larger flocs with higher settling rates. A number of methods have been employed to improve the settling characteristics of activated sludge. They include:

- Exposing the activated sludge to a limited concentration of a toxin such as ozone, chlorine or hydrogen peroxide, which preferentially kills the filamentous organisms (Larisch *et al.* 1997).
- Adding a polymer flocculent to aid in flocculation (Chen *et al.* 2001).
- Adding lime, or fine talc to the reactor, which can both aid in the production of biopolymers for flocculation, and increase the density of the flocs formed by inclusion of the heavy insoluble particles (Sanin *et al.* 2000; Wu *et al.* 2002).
- Biological methods (covered in more detail in the next section).

6.1.4 FOAMING IN BIOLOGICAL SYSTEMS

A foam is a gas in liquid dispersion where the bubbles of the gas phase are separated by thin films of liquid. Due to the very small thickness of the liquid films, foams can be considered as colloidal systems (Everett 1988), which were previously discussed in Section 5.1.2.1.
When the liquid films are stabilised by the presence of surface-active molecules such as detergents or amphipathic polymers (i.e. molecules which have one solvent soluble end and one end which is insoluble in the bulk solvent) they are known as micelles. These micelles are multi-layered with the inner layer having the same viscosity of the bulk liquid phase, while the two outer layers adjacent to the gas phase (which contain high concentrations of the surface active molecules) have a much higher viscosity. It is this high 'surface viscosity' that stabilises the dispersion (Bikerman 1973).

Generation of foams is a problem common to both the wool scouring industry and to aerobic treatment processes. Judging by problems experienced at Bremer Woll-Kämmerei AG with foam generation during aerobic treatment of wool scour rinse water (Hoffmann *et al.* 1996a), the likelihood of this problem occurring during aerobic treatment of Sirolan CF effluent is considered quite high.

Bendure (Bendure 1975) gives 10 ways to *increase* foam stability, among them are:

- Increase bulk liquid viscosity
- Increase surface viscosity
- Maintain thick walls (higher gas/liquid ratio in foam)
- Decrease liquid surface tension
- Reduce surfactant absorption rate
- Prevent liquid evaporation
- Avoid mechanical stresses
- Eliminate foam inhibitors

It follows that the opposite of each of these options leads to foam destabilisation or destruction.

Perry and Green (Perry *et al.* 1997) describe the following methods of foam destruction:

- Mechanical methods
- Pressure and Acoustic Vibrations

- Electrical Methods
- Thermal Methods
- Chemical Methods

Mechanical methods:

Rotating breaker bars are sometimes successful. It is best to combine their action with other methods and success can be improved by giving the foam sufficient time to build up foam height before hitting the breakers to enable the bubble walls to drain and weaken.

Wettability of the breaker rod is often critical. Generally a surface not wetted by the foam is superior – sometimes to the extent of using a porous media. Some cases have been observed (e.g. molasses) where a wax coated (easily wettable) surface was superior for foam breaking to a non wettable dry glass rod.

Subjecting foam to an air jet, can provide both mechanical stress as well as an element of drying and evaporation in the film, especially if the air is heated.

Pressure and Acoustic Vibrations:

High frequency pulses of air into the headspace of a sugar evaporator have been successfully used to control foam build-up. By oscillating the pressure in the headspace of the vessel, the foam bubbles are forced to contract and expand, the subsequent film flexing leading to accelerated bubble rupture (Perry *et al.* 1997).

High intensity sound has proven successful but expensive. Sonntag and Strenge cite effective foam suppression with 11kHz sound at 150db (Sonntag *et al.* 1972).

Electrical Methods:

Most foams have electrical double layers which contribute to foam stability. Although not many commercial applications have been developed, Sonntag and Strenge have shown that devices similar to electrostatic precipitators for dust removal (particularly where small plate spacings are used) can be particularly effective at destabilising the foam. A field strength in the order of 8 to 9 x 10^5 V/cm has been shown to be effective (Sonntag *et al.* 1972).

Thermal Methods:

Many foams have a critical temperature, above which the foam becomes fast draining due to the decrease in film surface viscosity. The surface viscosity is so temperature sensitive that at

the 'critical temperature', the drainage rate of the foam may increase up to a hundred fold over the space of a few degrees.

Thermal methods have been seen to be most effect when combined with a mechanical breaker, which takes advantage of the thermal weakening of the film. A variety of methods for achieving this are in use including:

- A rotating paddle combined with the heating system
- Hot water spray onto the foam
- A jet of hot air which combines heating, evaporative drying and mechanical stress of the film
- A jet of process steam onto the foam headspace
- Direct gas fired heating in the headspace of the foam generation vessel

Bikerman (Bikerman 1973) attributes drop in 'foaminess' of the liquor with temperature to an increase in the solubility of the surfactant compounds. He also suggests the influence of evaporation and viscosity as significant to the drainage rate, but fails to quantify these or provide supporting experimental results.

Chemical Methods:

This is the most common practice for both foam prevention (anti-foam) and foam destruction (de-foamers). When applied to biological treatment systems however, great care must be taken before deciding to use, and in selecting either of these chemical additives. Many of the commercially available products can prove biocidal and thus detrimental to the effectiveness and robustness of the treatment plant. There are also the issues of biodegradability. If the chemical is easily biodegradable, it will be broken down in the digester before it can act effectively, whereas if the chemical is not biodegradable at all it may contribute to and increase the contaminant loading (COD) discharged to drain from the reactor.

Solutions to these problems do exist, particularly products specifically designed for use in bioreactors. By using an immiscible product that floats on top of the liquid in the reactors (combined with an under water effluent draw-off) anti-foam retention is provided and only very small amounts escape with the product.

In the majority of cases the chemicals used are actually dispersed throughout the solution. As their concentration is generally in the ppm range, this is often not an overly significant contributor to effluent COD, but the cost issue may still remain significant.

Biological Control of Filamentous Foaming and Bulking:

Eckenfelder (Eckenfelder 1992) states that filamentous bacteria have been shown to cause both bulking in the settling system of the activated sludge system, and excessive foam production in the aeration vessel. Others (Harris *et al.* 1975; Magara *et al.* 1976; Steiner *et al.* 1976) also attribute these phenomena to the build-up of extracellular biopolymers by some micro-organisms, with insufficient extracellular biopolymer causing discrete dispersed growth and too much causing 'slime layer bulking'.

A standard (if somewhat subjective) test used for quantification of filament abundance is to use a 100 x magnification micrograph of the biological floc and count the number of filaments present.

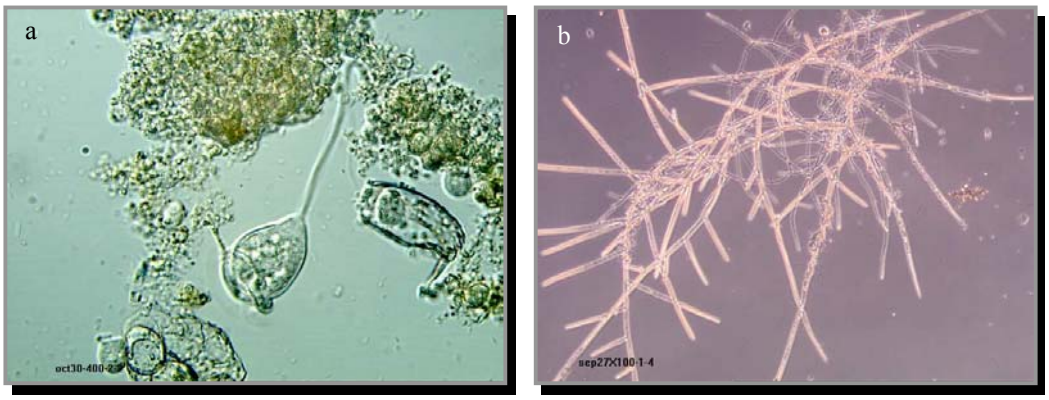


Figure 6.12 a) Non filamentous organisms (100 x Magnification) b) filamentous organisms (100 x Magnification)

The abundance of filamentous organisms is then classified according to Table 6.3 (Eckenfelder 1992).

Table 6.3 Abundance of filamentous organisms

Numerical Value	Abundance	Explanation
0	None	
1	Few	*Filaments present but only observed in an occasional floc*
2	Some	*Filaments commonly observed but not present in all flocs*
3	Common	*Filaments observed in all flocs but at low density (e.g. 1 to 5 filaments per floc)*
4	Very Common	*Filaments observed in all flocs at medium density (e.g. 5 to 20 per floc)*
5	Abundant	*Filaments observed in all flocs at high density (e.g. 20 per floc)*
6	Excessive	*Filaments present in all flocs , appears more filaments than flocs and/or filaments growing in abundance in bulk solution*

F class (foaming) filamentous bacteria produce bio-surfactants and have a hydrophobic cell membrane, which enables them to froth and create scum.

A scum index is also proposed by Eckenfelder (Eckenfelder 1992), in order to facilitate quantification of the foaming potential of the biological culture.

$$\text{Scum Index (SI)} = \frac{\text{mass of biomass in foam}}{\text{total mass of biomass}} \times 100\% \qquad (45)$$

Standard results are obtained by bubbling $10 m^3/hr_{air}$ per $m^3_{effluent}$ through the sample and separating off the foam fraction until no foaming agents are left in the sediment phase. From these results the following conclusions can be drawn:

Table 6.4 Qualitative evaluation of foaming in biological systems

SI %	Extent of Foaming Problems
0 – 0.5	Negligible
0.5 – 6	Small
6 – 10	Medium
10 – 15	Serious
>15	Catastrophic

Eckenfelder goes on to give two generic approaches to controlling the growth of undesired filamentous organisms:

(1) Biological methods aimed at suppressing the growth of filamentous organisms
(2) Non – specific control methods of treating the consequences of the filamentous biological growth

The first approach in particular should be considered in the plant design phase, whereas the latter (extensively detailed below) is more often used as a 'bolt on cure' when the problems are encountered after the plant has been commissioned.

Once identified, biological foaming can be initially reduced in the plant design phase by preventing entrapment or recirculation of the foam. This can be simply achieved by using a separate foam draw-off and not recombining it with the recyle activated sludge stream.

A useful review of the relationship between filamentous and non-filamentous organisms under anoxic conditions is given by Albertson (Albertson 1991). Due to the morphology of the cells, any growth limiting conditions such as lack of nutrients (primarily NH_4^+ and PO_4^{2-}), low dissolved oxygen, or low BOD_5 will all favour growth of filamentous bacteria which can best utilise these scarce commodities.

The key method of controlling such undesired growth is to introduce a substrate concentration gradient into the reactor system. This can be achieved by:

- Using a plug flow reactor with limited axial mixing
- Installing one or more baffles in the complete mix CSTR tank
- Using a pre-selector or contact tank to expose the return activated sludge to a high concentration of substrate, thus encouraging healthy floc formation before it is fed into back into the main reactor.

The latter is the generally the preferred option for high strength industrial wastes due to its simplicity and versatility. In the case of the wool scour effluent being treated, the key problem that requires overcoming in application of this principle is the return activated sludge (RAS) recycled from the clarifier suffering pH shock when it encounters the low pH of the Sirolan CF pre-treated effluent. The most obvious method for dealing with this is to recycle

sufficient volume of RAS (pH ~8.2) to neutralise the incoming Sirolan CF effluent (pH ~4.0) to pH > 6.5.

It must be noted that this high hydraulic recycle will triple the flow passing through the system and feed pumps must be sized accordingly. Although the increased flow is passing out the underflow of the gravity settler and therefore should if anything improve the clarifier performance, the hydraulic effects of this increase in overall flow must be carefully considered as part of the clarifier design process.

The ability of the selector zone to suppress filamentous growth in the main reactor is explained not only by optimising the growth rate of the desired micro-organisms while in the selector zone, but also by taking advantage of another property of these bacteria. The desired floc forming bacteria have the ability to store nutrients and substrate (BOD_5 contributing compounds) for later use when exposed to lower concentrations of these compounds (Daigger *et al.* 1992), thus allowing them to compete against the filamentous bacteria in the main reactor. Anaerobic selectors in particular, select for phosphate accumulating bacteria and thus provide increased phosphate uptake (and subsequent removal) from the waste-water being processed (Randall *et al.* 1992).

In the case of a high volumetric recycle of RAS from the settling basin, as suggested for the treatment of low pH wool scour effluent, the high flow of aerobically treated liquid entrained with this sludge would lead to anoxic conditions in the selector tank.

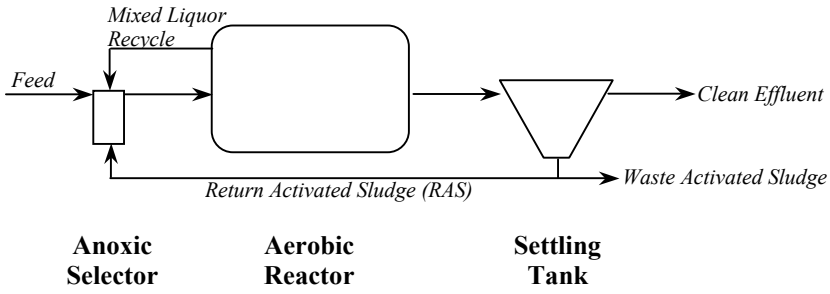


Figure 6.13 Activated sludge process with anoxic selector

An Anoxic Selector should be designed so that there is sufficient total recycle (RAS Sludge + aerobically treated liquor) to maintain pH > 6.5 in the selector. The recycle rate is usually minimised to give highest possible substrate concentration in the selector, but in the case of

wool scour effluent, the waste strength is sufficiently strong that this is more likely to cause problems with bio-inhibition and toxic shock to the bacteria. Maintaining a neutral pH in the selector is likely to prove to be the key design criteria.

Usefulness of an Anoxic Zone other than as a Selector:

- In an *Oxic* (or aerobic) system such as the traditional activated sludge process, molecular oxygen is used as the 'terminal electron acceptor' or oxidising agent to destroy the BOD_5 in the wastewater (Figure 6.4). In this system the bugs effectively breathe oxygen just like humans.

- In an anoxic system the nitrate content of the liquor from the aerobic reactor is used as the terminal electron acceptor in microbial respiration. In this system the bugs breathe nitrate while they eat the BOD_5. This is called de-nitrification.

- The anoxic effluent then flows into the aerobic reactor (Figure 6.13) where nitrification occurs. Nitrification involves the conversion of ammonia-nitrogen to nitrite then nitrate-nitrogen (which can be recycled to the anoxic zone and converted to molecular nitrogen gas by the de-nitrification process).

The net effect is the conversion of ammonia (a significant pollutant which builds up in scouring effluents) and nitrogen oxides (NO_X, which contribute strongly to the BOD_5) to atmospheric nitrogen, which is air-stripped into the off-gas leaving the aerobic reactor.

The carryover of filamentous organisms in the clarifier supernatant is often addressed by adding flocculent or precipitants to the aeration basin. One commonly used precipitant is lime, which has been observed to improve the structure and settling properties of biological flocs (Daigger *et al.* 1992). Lime addition into the small anoxic tank prior to the main activated sludge aeration vessel would therefore partially reduce the pH stress on the RAS, while potentially improving the settling characteristics of the activated sludge.

Once a foam or scum is established, Eckenfelder (Eckenfelder 1992) suggests that use of dispersed anti-foams and bio-toxins in aeration vessels and secondary settlers is usually ineffective due to the concentration of organisms growing within the foam. Due to the weight of biological foams, water sprinklers are often also reported to have very limited effect.

In this light the best method for treating the problem is likely to be selectively removing the foam from the top of the vessel, and not re-combining it with the recirculated RAS sludge stream.

6.2 EXPERIMENTAL PROCEDURE

The goal of the laboratory scale experiments carried out in the 5L Bioflow3000 reactor was to verify the effectiveness of a continuous mix aerobic activated sludge process biologically treating acidic wool scouring effluent pre-treated by the Sirolan CF chemical flocculation process. This investigation was also aimed at collecting sufficient rate data to develop a kinetic model of the reactions involved.

The experimental work carried out on the proposed activated sludge process was performed at three different levels: Laboratory scale, pilot plant scale and demonstration plant scale.

The initial feasibility study and bio-kinetics investigations were carried out under strictly controlled laboratory conditions. For these studies a 5 litre Bioflo3000 bench top fermenter was used.

6.2.1 APPARATUS

The reactor was set up to operate as a continuous flow stirred tank reactor consisting of:

- A sealed 5L glass vessel
- A diaphragm air pump
- A variable speed mixer (6 bladed disc turbine)
- A heat / cool temperature control jacket
- Dissolved oxygen monitoring
- Computer controlled peristaltic feed and sludge recycle pumps
- A separate solids settling vessel.

The reactor was set up as in Figure 6.1 with gravity flow of effluent from the reactor vessel to the settler and from the settler to drain. The physical reactor set-up is shown in Figure 6.14 and Figure 6.15.

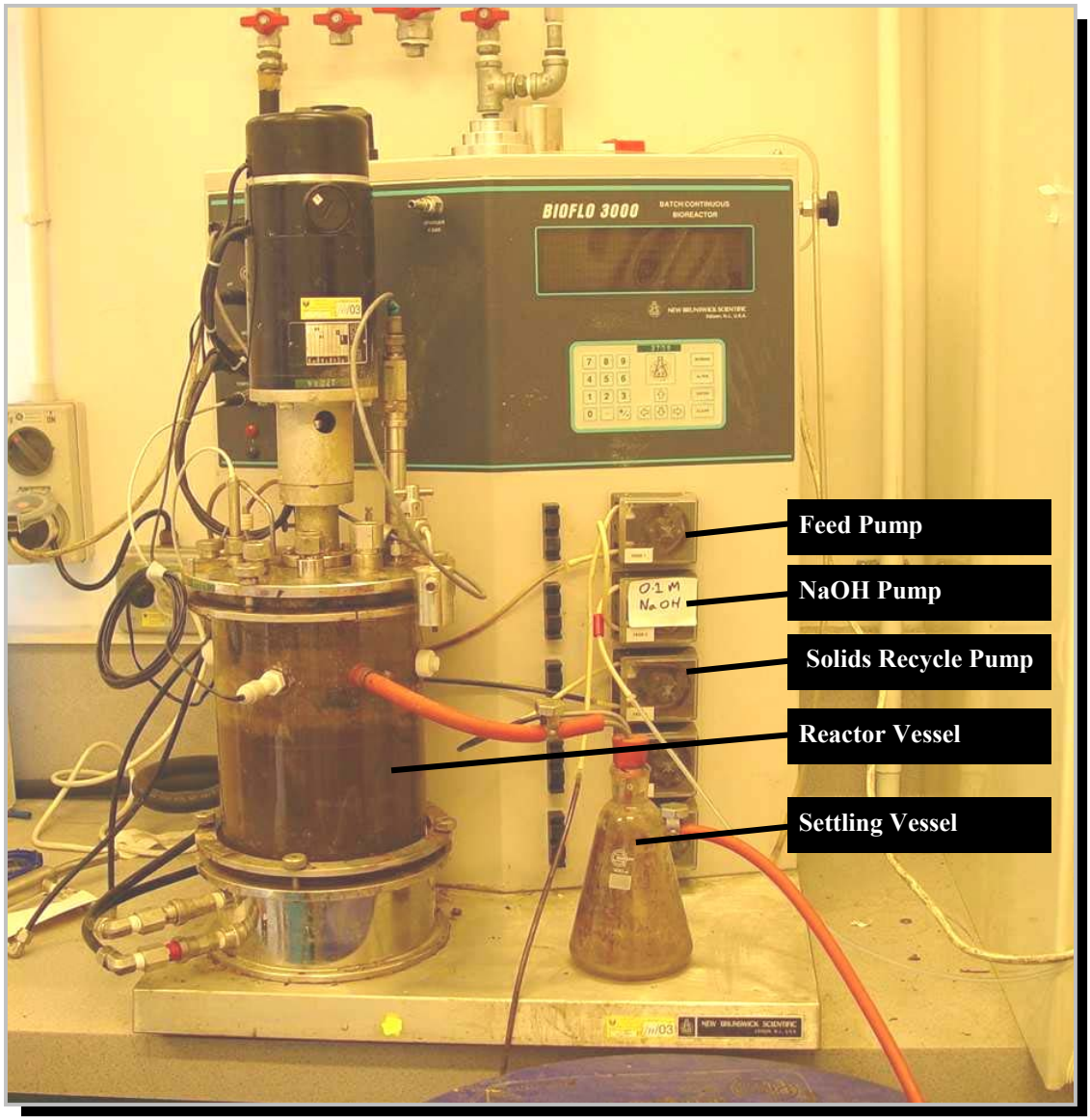


Figure 6.14 5 Litre Bioflo3000 continuous fermentation reactor

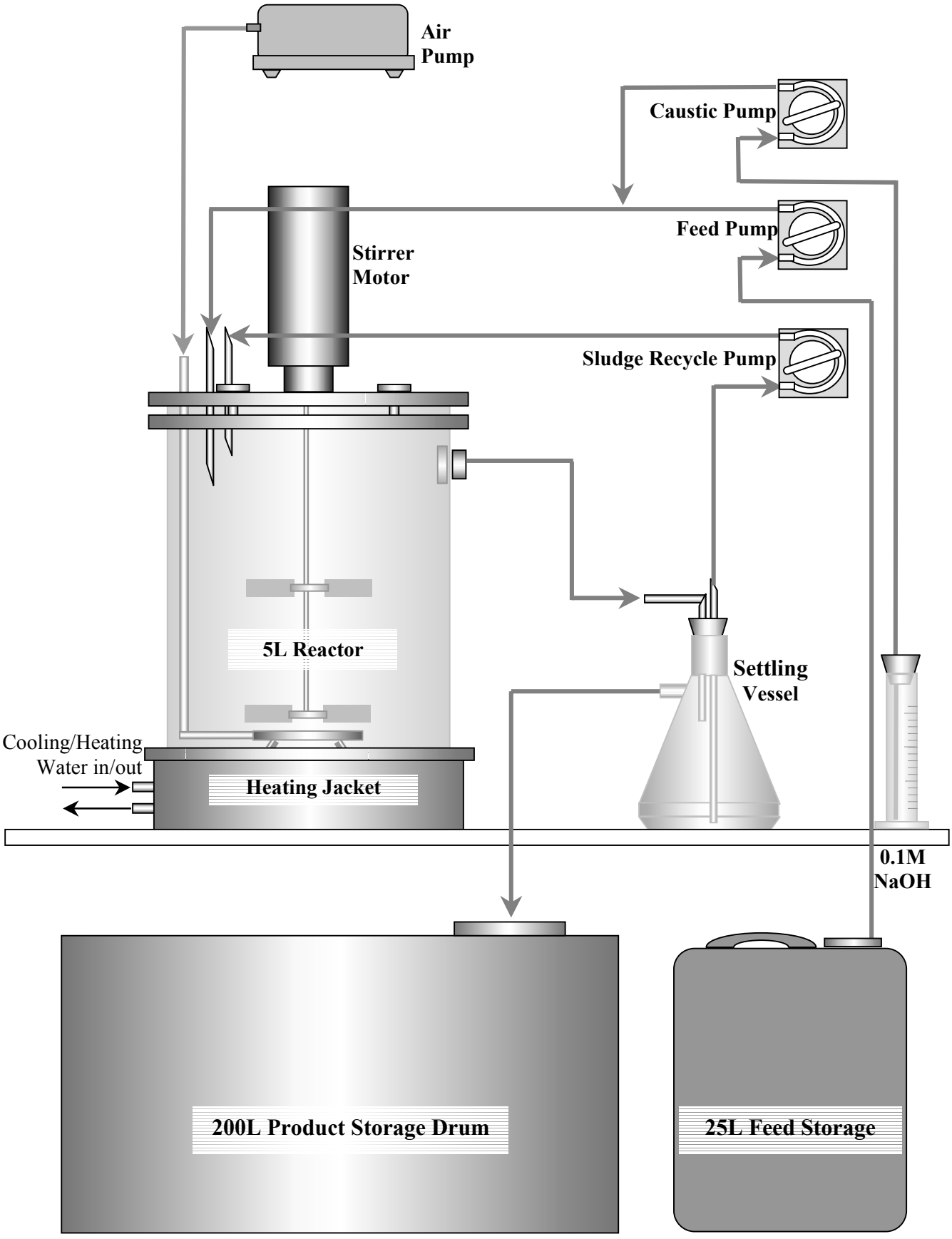


Figure 6.15 Bioflo3000 bench top reactor

For the laboratory scale testing a Bioflo3000 bench top reactor was used as detailed above. To ensure consistent feed quality, 50L of Sirolan CF centrate was collected at a time and fed to the reactor from 25L bulk chemical containers. Once the effluent had passed through the reactor and settling vessel the processed effluent was collected in a 200L drum for disposal.

6.2.2 SEEDING PROCEDURE

To ensure consistency between experiments and validity of the first trials carried out, the biological reactor had to be seeded and the resultant microbial culture acclimatised to the feed effluent before any actual experimentation could be carried out. This involved growing a microbiological culture in the reactor and allowing it to adapt to the type of feed that would be used in the experimental trials. Rather than use a bacterial feedstock from another source such as a municipal activated sludge water treatment plant, it was decided to grow a biological culture based on the micro-organisms that were naturally occurring in the wool scouring effluent. To achieve this the 5L reactor was filled with the following mixture:

- 1.0L of Sirolan CF liquor (to which the activated sludge is to become acclimatised)
- 3.3L of 30°C tap water (to dilute the Sirolan CF centrate to a level more likely to be found in an operational continuous flow reactor)
- 0.5L of 10% Glucose solution (to act as a readily degradable food source for rapid biological growth)
- 0.2L of stagnant effluent collected from the site outfall sump of an operational wool scour (this sample is likely to contain a prolific culture of the micro-organisms present in raw wool scouring effluent)

The mixture was then neutralised to pH 7.0 by addition of concentrated caustic soda, and the aeration and temperature control systems set into operation.

The suspended solids content of the mixture was monitored daily and once microbial growth had been detected (as measured by an increase in the suspended solids concentration from 500 to 1,700mg/L), 12mL per hour of straight Sirolan CF centrate was fed to the reactor via the peristaltic feed pump. This caused the contents of the reactor to overflow into the settling vessel, from which the settled solids were pumped back to the reactor vessel and the supernatant allowed to overflow to drain. The pH of the system was monitored as the Sirolan CF centrate (pH 3.5) was added, and when after five days of this operation no decrease in reactor pH had occurred the feed rate was increased up to 65mL per hour, approximately half

the expected operational feed rate based on the 36 hour residence time recommended by the Australian CSIRO (Bateup *et al.* 1996).

For the first two days of operation at this increased feed rate, addition of small quantities of caustic soda were required to maintain reactor pH > 7.0. By the fourth day the pH of the reactor had stabilised to 8.2 with no further caustic soda addition required under normal operating conditions. After a total of 15 days had passed since start-up, the reactor was still running stably with no caustic soda addition required. It was decided at this point that the microbial culture was acclimatised to the feed substrate.

6.2.3 INITIAL REACTION RATE AND PROCESS FEASIBILITY EXPERIMENTS.

In order to establish initial reaction rates and an overview of the bio-chemical reaction kinetics involved in the process, an initial set of tests were carried out using the Bioflo3000 bench top fermentation reactor.

In the first set of experiments, the temperature, pH, mixing and aeration rates of the reactor were all held constant while substrate feed concentrations and hydraulic residence time were varied according to the parameters given in Table 6.5.

Table 6.5 Initial kinetic analysis parameters

Hydraulic Residence Time	Feed Strength (BOD_5)
75 Hours	3,500 mg/L
	4,600 mg/L
	7,800 mg/L
	9,600 mg/L
50 Hours	1,600 mg/L
	1,700 mg/L
	2,500 mg/L
	3,100 mg/L
	3,300 mg/L
	4,000 mg/L
	4,600 mg/L
36 Hours	1,200 mg/L
	3,400 mg/L
	4,200 mg/L

Prior to the first tests being carried out, the reactor was seeded as detailed previously to ensure the presence of a stable biological culture. The first tests were carried with a 75 hour hydraulic residence time in the reactor, as this corresponded to the feed rate of 65mL/hr used during the final phase of reactor seeding and the reactor was already operating in a stable manner at this feed rate.

After any feed rate or feed concentration parameter was altered, the reactor was operated continuously under the new process conditions for ten days to enable pseudo steady-state conditions to develop in the reactor before any product analysis was carried out.

All feed effluent of BOD_5 higher than 6,000mg/L was undiluted Sirolan CF effluent with the different BOD_5 levels arising from day to day changes in the effluent quality produced by the Sirolan CF process used to generate the feed liquor. All trials with feed BOD_5 levels below 6,000mg/L were achieved by diluting a bulk quantity of raw Sirolan CF liquor with tap water until the desired feed concentration was achieved. This was considered necessary as Sirolan CF effluent produced elsewhere in the world (particularly from the processing of Australian wool scouring liquors) is typically of significantly lower BOD_5 and COD than that which the Fairlie Wool Scour Sirolan CF plant was able to produce. This wide range of feed concentrations also allowed a better idea of the process kinetics to be established from these early trials.

After the reactor had been allowed ten days operation to achieve steady-state, samples of the product were analysed for BOD_5, Suspended Solids and pH as per Section 3. These values were used, along with corresponding analysis for the feed effluent, to develop reaction rate data and kinetic models for the biological system.

6.2.4 SUBSTRATE INHIBITION TESTING

After initial kinetic analysis suggested that there was some inhibition of reaction rate with increasing feed strength (detailed later in Section 6.3.1), specific tests were carried out to positively identify any substrate inhibition that may have been occurring.

6.2.4.1 Selection of test method

The two types of test procedure used to quantify activity rate of the activated sludge culture were based on measurement of glucose and oxygen uptake respectively. The glucose inhibition procedure involved measuring uptake of glucose by the aerobic bacteria under varying concentrations of the inhibitive substrate. This test procedure was carried out based on the procedure developed by Larson (Larson *et al.* 1982) but complications were encountered with the feed substrate interfering with the glucose analysis procedure. This procedure proved unreliable and gave results that could not be reproduced.

Respirometric analysis however, which used a dissolved oxygen probe to measure oxygen uptake rate of the microbial culture under differing substrate concentrations proved both reliable and repeatable.

6.2.4.2 Respirometric Test Procedure

In this analysis, samples of mixed liquor containing an aerobic microbial culture acclimatised to the substrate to be tested were oxygen saturated, then added to an oxygen saturated substrate – water mixture. The dissolved oxygen content of this mixture was then measured with time by using an Ingold InPro6200 silver electrode dissolved oxygen probe in a beaker continuously stirred by a magnetic stirrer. The magnetic stirrer was maintained at a constant speed of 250rpm. This was sufficient to give approximately 0.2m/s liquor flow over the sensor head of the dissolved oxygen probe without causing sufficient surface turbulence to accelerate oxygen transfer into the liquor. The test apparatus is shown in Figure 6.16 below.

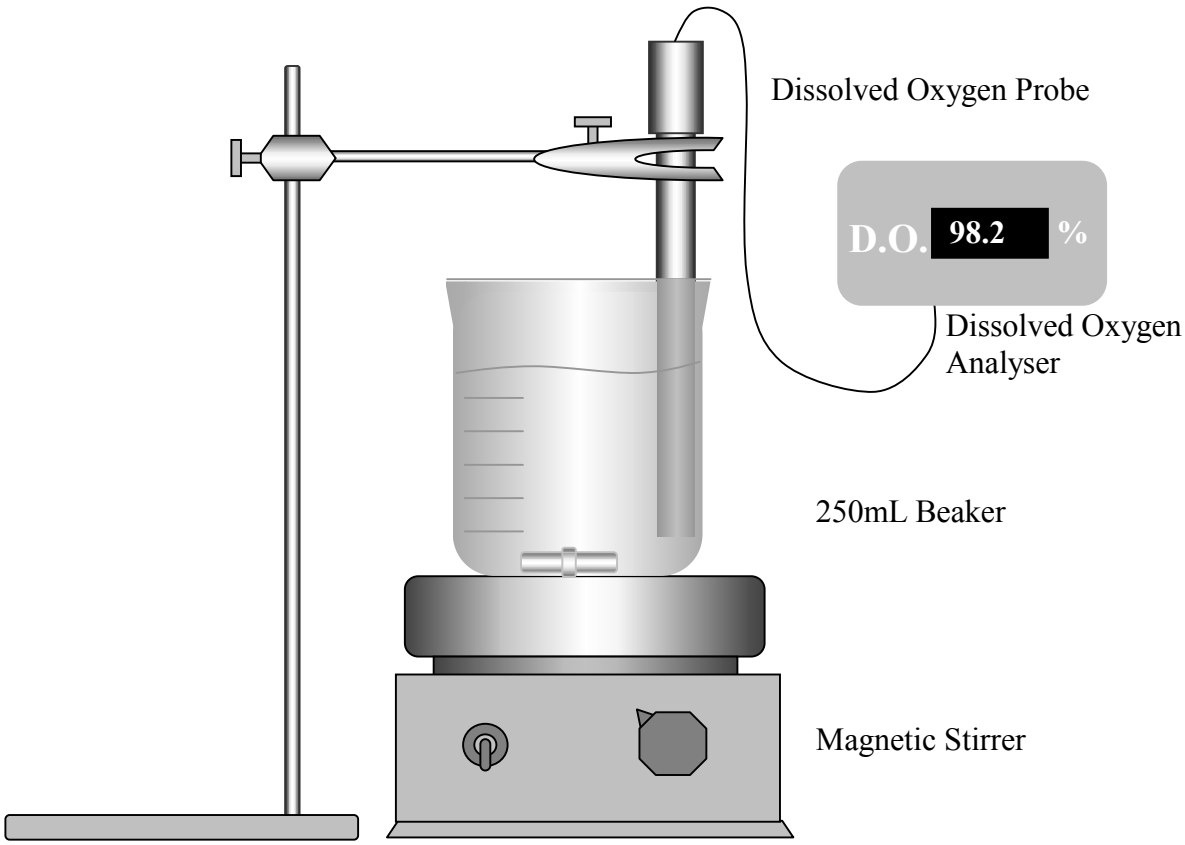


Figure 6.16 Respirmetric inhibition testing apparatus

The samples tested for Substrate inhibition consisted of the following mixtures:

Table 6.6 Sample compositions used for substrate inhibition testing

Sample Number	Biological Mixed Liquor	Distilled Water	Feed Substrate
1	100mL	100mL	0mL
2	100mL	75mL	25mL
3	100mL	50mL	50mL
4	100mL	25mL	75mL
5	100mL	0mL	100mL

The substrate – distilled water mixture was oxygen saturated prior to each test run by sparging with air in a gas wash bottle connected to a vacuum pump as shown in Figure 6.17.

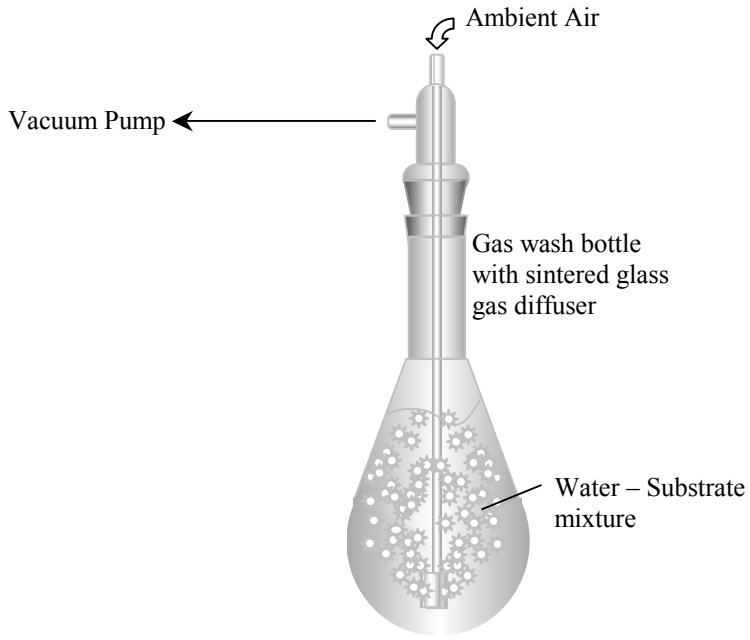


Figure 6.17 Apparatus used for oxygen saturation of liquor samples

The mixed liquor in the bench top Bioflo3000 reactor was also oxygen saturated prior to testing. This was achieved by increasing the speed of the gas distribution impeller (Figure 6.15) to 300% of its normal mixing speed for approximately 20 minutes prior to the analysis being carried out.

Once the water – substrate mixture had been saturated with dissolved oxygen it was added to the beaker of the analysis apparatus pictured in Figure 6.16. Once the dissolved oxygen concentration measured in this liquor had stabilised, 100mL of mixed liquor was extracted from the aerobic reactor and immediately added to the beaker containing the substrate – water mixture. The addition of the biologically active mixed liquor was taken as time zero, and the dissolved oxygen concentration of the resulting mixture was measured every 60 seconds for at least the next 10 minutes.

The rate of oxygen uptake by the biological culture over this time period was then calculated for each substrate concentration. Conclusions drawn about the inhibitive properties of the substrate at these different levels were based on suppression of oxygen uptake by the aerobic culture.

6.2.5 pH INHIBITION TESTING.

In order to isolate any effect that the low pH of the substrate (typically pH3.0 – 3.6) was having on the results of the substrate inhibition tests carried out above, two further sets of analysis were carried out to positively identify:

a) The inhibitive effect of substrate concentration at pH7.0
b) The inhibitive effect of low pH on the biological culture in the absence of excess substrate.

6.2.5.1 Substrate inhibition at pH 7.0

Firstly the substrate inhibition tests carried out in Section 6.2.4 above were repeated with Sirolan CF effluent that had been neutralised to pH 7.0 with sodium hydroxide prior to testing.

Samples were again made up as per the details given in Table 6.6, using the same bulk sample of Sirolan CF centrate as used in substrate testing, but this time neutralised to pH 7.0.

The dissolved oxygen concentration was again measured with time, and the effect of Sirolan CF centrate concentration, in the absence of excess acidity, determined.

6.2.5.2 pH inhibition in the absence of excess substrate

For this analysis the same procedure was used as detailed in Section 6.2.4 above. In this instance however, the biologically active mixed liquor samples were exposed to mixtures of distilled water and dilute sulphuric acid rather than the Sirolan CF centrate feed stock used previously.

The composition of the samples used for pH inhibition testing is detailed in Table 6.7.

Table 6.7 Sample compositions used for pH inhibition testing

Sample Number	Biological Mixed Liquor	Distilled Water	1% H_2SO_4
1	100mL	25mL	0mL
2	100mL	24mL	1mL
3	100mL	23mL	2mL
4	100mL	22mL	3mL
5	100mL	21mL	4mL
6	100mL	19mL	6mL
7	100mL	17mL	8mL

Once again, the water – acid mixture was oxygen saturated using the apparatus in shown in Figure 6.17 and added to the beaker of the dissolved oxygen measurement apparatus. Once the oxygen level had stabilised, the biological mixed liquor was added and timing commenced.

6.2.6 MECHANICAL DEVICES FOR FOAM CONTROL

Based on the positive results achieved by using a simple mechanical foam breaker in the 5,000L pilot plant reactor (detailed in Section 7.4.4), investigations were carried out at laboratory scale to investigate the effect of different mechanical foam breaker configurations.

Several geometries and sizes of perforated plate (Figure 6.18) were installed in a bucket fitted with a sintered glass aeration device (Figure 6.19) and filled with the mixed liquor from the aerobic reactor. The sections of perforated plate were then rotated at a range of speeds in order to apply shear force to the foam produced and promote collapse of the micelle structure.

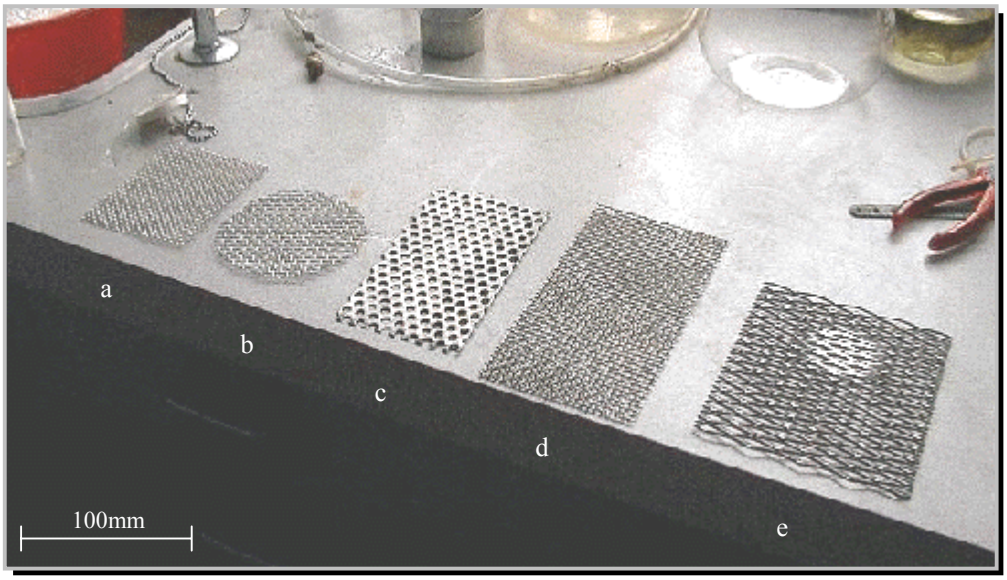


Figure 6.18 Impellers trialled for mechanical foam destruction

Figure 6.19 Foam generation device

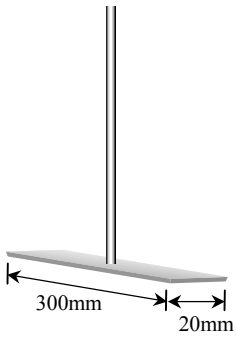


Figure 6.20 Perspex blade used in foam breaking trials

In a further trial carried out after those involving the perforated plates, a Perspex blade (Figure 6.20, Figure 6.33a) was fitted to the rotating shaft of the foam breaker test apparatus, and its foam breaking ability compared to that of the perforated plates.

6.2.7 SLUDGE QUALITY ANALYSIS

In order to evaluate the quality of the biomass in the Bioflo3000 reactor, phase contrast micrographs were taken of the reactor mixed liquor at 100x and 1000x magnification using an Olympus BX60 trinocular microscope with a standard 10x / 0.30BD objective lens and a 100x

/ 0.90BD oil immersion objective lens connected by an Ikegami black and white CCD video camera to a PC operating Optimas 6.51 video capture software. The resulting micrographs were evaluated optically for the quality of biological flocs formed, and the general types of micro-fauna present (See Table 6.3).

6.3 RESULTS

6.3.1 INITIAL KINETIC DATA

Tests carried out with consistent feed quality in the bench-top Bioflo3000 reactor typically yielded lower substrate removal results than those reported by the CSIRO for the same system. (Bateup *et al.* 1996). Both investigations used the Sirolan CF Process with sulphuric acid and Profloc CX-533 polymer flocculent to treat the heavy wool scour effluent prior to being fed to the biological reactor.

As the key difference between the Australian CSIRO investigation and that carried out in New Zealand was the concentration of substrate in the feed (illustrated by the BOD_5 and suspended solids levels in Table 6.8 below), an investigation was carried out into the effect of feed concentration.

Table 6.8 Sirolan CF pre-treated feed to the biological reactor

Feed Source	**BOD_5**	**Suspended Solids**
Australian Scour Effluent*	1,100 – 2,100 mg/L	70 – 300 mg/L
New Zealand Scour Effluent	3,000 – 9,000 mg/L	600 – 3,000 mg/L

*(Bateup *et al.* 1996; Poole *et al.* 1999)

Table 6.9 Results of the Bioflo3000 laboratory reactor trials

HRT [Hours]	Feed BOD_5 [mg/L]	MLSS [mg/L]	Product BOD_5 [mg/L]	BOD_5 Removal
75	9600	3700	860	91%
75	7800	3700	1200	85%
75	4600	3500	140	97%
75	3500	2100	460	87%
75	3000	430	72	98%
50	6100	7200	150	98%
50	4600	1800	1100	76%
50	4000	1300	210	95%
50	3300	970	140	96%
50	3200	1200	140	96%
50	3100	910	140	95%
50	2500	430	370	85%
50	2300	490	170	93%
50	1700	1200	310	82%
50	1600	570	130	92%

For a 50 hour hydraulic reaction time, the specific substrate removal rate (mg of BOD_5 removed per mg of biomass at a fixed residence time) in the Bioflo3000 reactor was shown to decrease with increasing concentration of feed to the reactor. As shown by Figure 6.21, this is most evident in the feed BOD_5 range most commonly encountered under New Zealand operating conditions [$3{,}500 < BOD_5 < 6{,}500$].

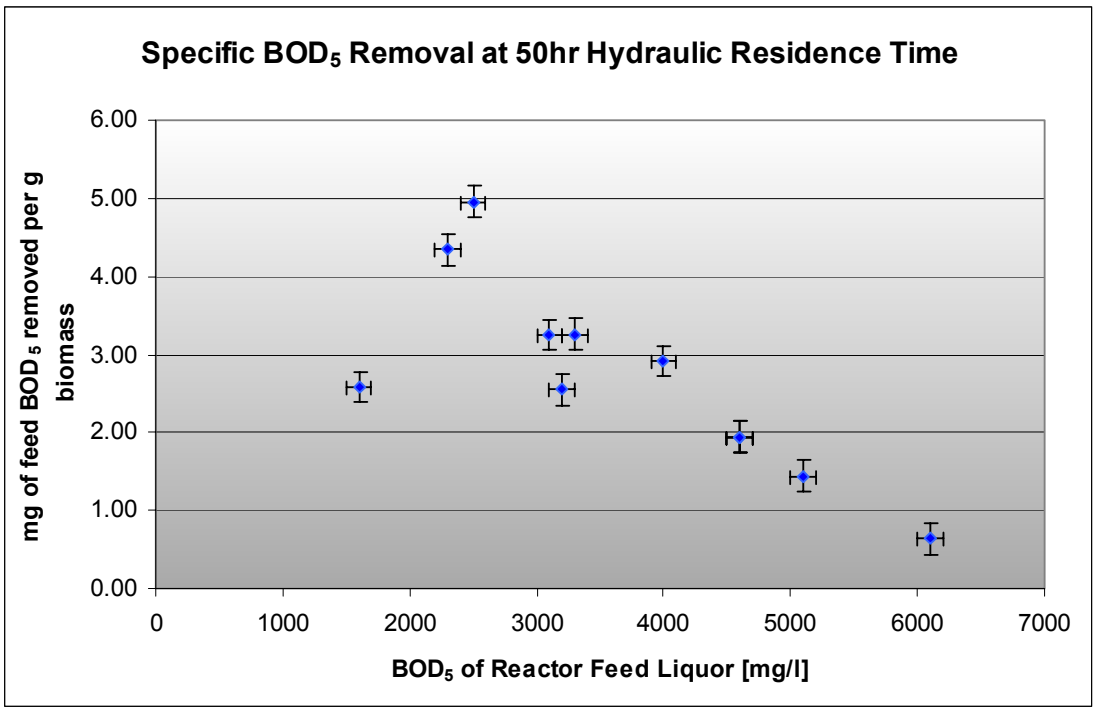


Figure 6.21 Specific BOD_5 removal with feed concentration

At feed substrate concentrations above 6,500mg/L BOD_5, the biological reactor did not operate self sufficiently at a hydraulic residence time of 50 hours, requiring regular dosing of caustic soda to prevent reactor pH from dropping below the level required to maintain biological growth. At feed concentrations of 6,500 – 9,000mg/L BOD_5, approximately 0.04 – 0.05g of Caustic Soda (100% active basis) was required per litre of effluent processed to maintain optimum operating pH of $pH > 6.8$

As can be seen from Figure 6.21, above a feed concentration of approximately 3,000mg/L BOD_5, the specific substrate uptake rate consistently decreases as the feed concentration increases. Figure 6.22, which is based upon the same dataset as Figure 6.21 shows that this transition corresponds to a reactor mixed liquor substrate concentration in the range 400 – 500mg/L BOD_5, above which the microbial substrate uptake rate steadily decreases.

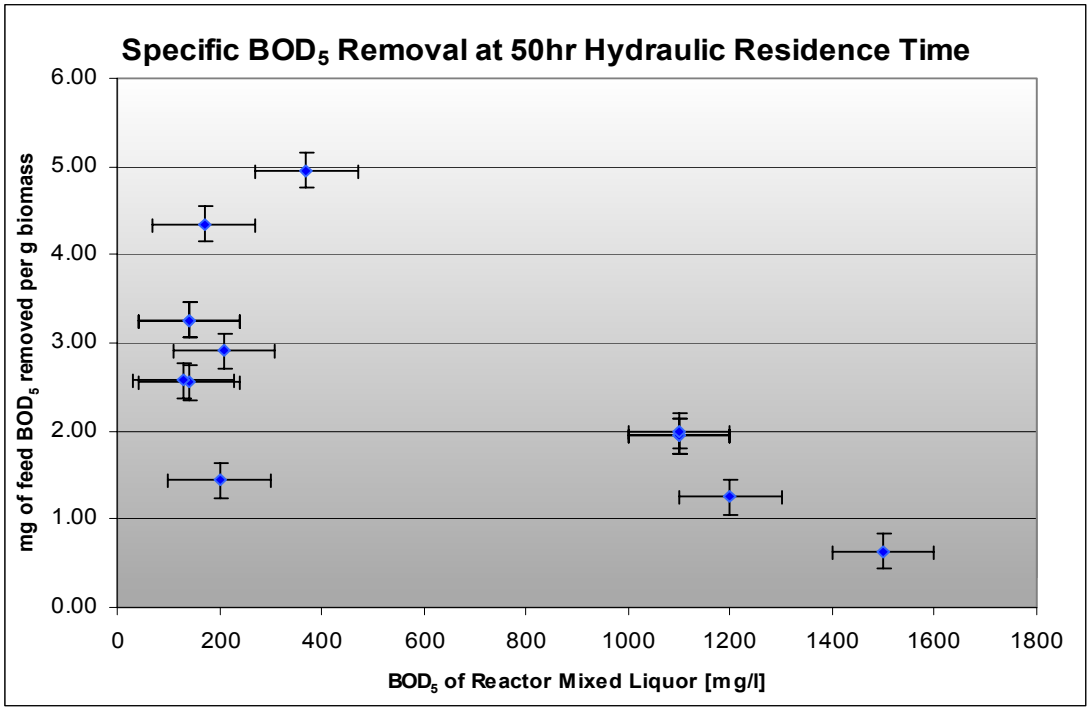


Figure 6.22 Specific BOD_5 removal with reactor substrate concentration

6.3.2 SUBSTRATE INHIBITION RESULTS

As identified by initial kinetic testing, at high concentration levels the substrate feed to the bioreactor does in some way inhibit biological activity in the digester vessels (Figure 6.22). To verify and empirically quantify this, testing was carried out on the effect of various substrate concentrations on the respiration rate of the mixed biological culture. To achieve this, a closed respirometry cell was used as detailed in section 6.2.4. This cell enabled the oxygen uptake rate (and hence metabolic activity) of the biological cultures to be determined under various environmental conditions.

The first experiment carried out was aimed at determining the effect of increasing substrate mixed liquor concentration (measured as COD) on the respiration rate of an acclimatised mixed biological culture. The resultant oxygen uptake rates measured are illustrated in Figure 6.23.

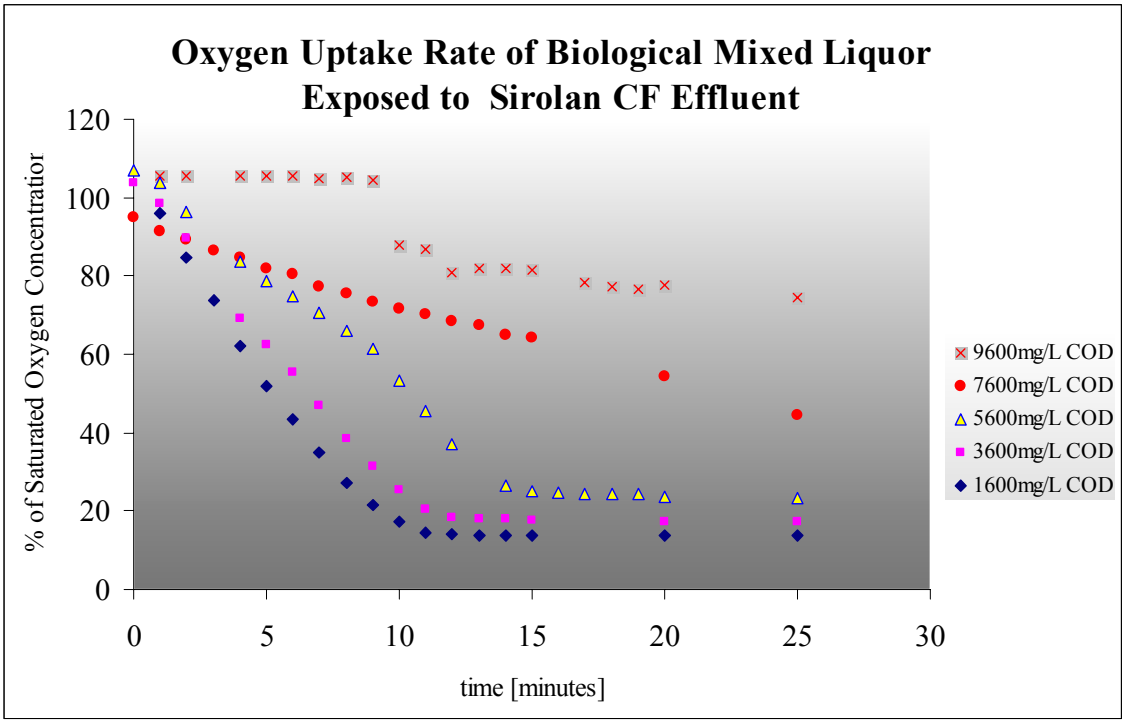


Figure 6.23 Oxygen uptake of biological culture exposed to Sirolan CF liquor

Figure 6.23 shows a marked decrease in the oxygen uptake of the mixed culture as the substrate concentration in the respiration cell was increased. The 1,600mg/L COD dataset in Figure 6.23 demarked by the "◆" data points was the control run and represents the uninhibited respiration rate of the biological culture with no excess of unmetabolised Sirolan CF liquor present.

To enable the correlation of the data presented in Figure 6.23 with that published by others (Ryssov-Nielsen 1975; Larson *et al.* 1982; Torrens *et al.* 1999) the average oxygen uptake rate over the first ten minutes of the test was calculated and used as the maximum respiration rate. The effect of substrate concentration on maximum respiration rate clearly shows decreasing biological activity with increased mixed liquor COD. By taking the control run (COD = 1,600mg/L, no CF liquor added) as 0% inhibition, and the point where all respiration ceases as 100% inhibition, the following relationship can be drawn from the data presented in Figure 6.23:

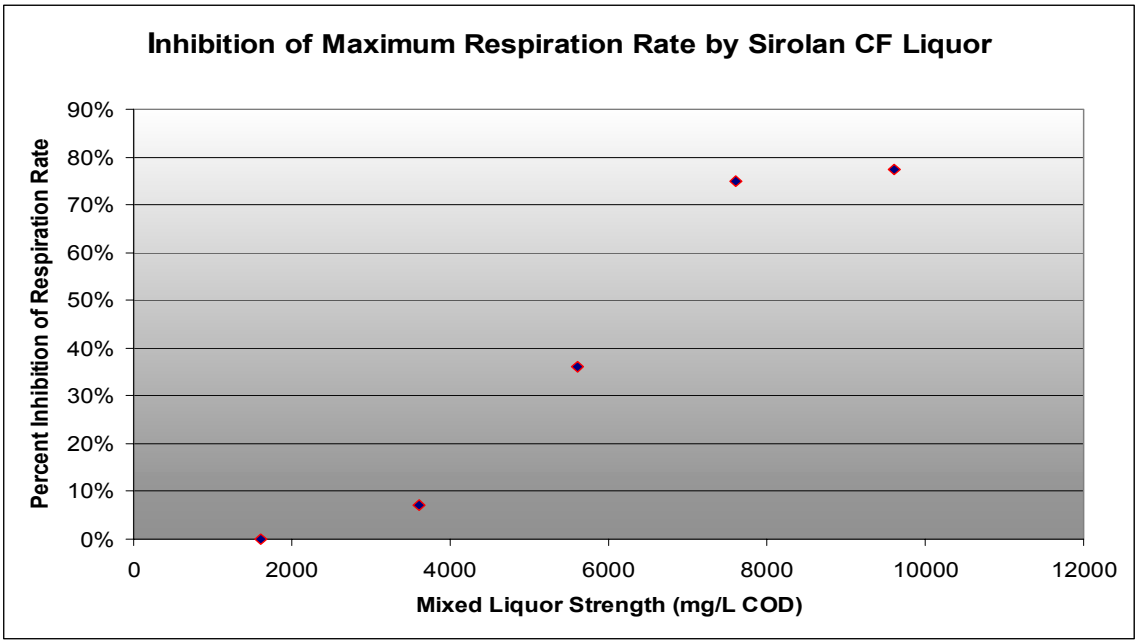


Figure 6.24 Inhibition of respiration rate by Sirolan CF liquor

The results illustrated by Figure 6.23 and Figure 6.24 confirm that the raw Sirolan CF feed to the biological system inhibits substrate metabolism in the mixed biological culture with as much as 79% inhibition occurring at just below 10,000mg/L COD.

6.3.3 pH Inhibition Results

In order to isolate the contribution of the acidity of the low pH feed to the inhibition that has been verified as occurring, two more respirometry tests were carried out as detailed in sections 6.2.4 and 6.2.5.

6.3.3.1 Inhibition by Neutralised Sirolan CF Effluent

Initially the experiments detailed above were repeated with neutralised (pH = 7.0) Sirolan CF effluent as the feed. Inhibition of initial respiration rate (over the first 10 minutes of respiration) by the neutralised effluent is illustrated in Figure 6.25 overleaf.

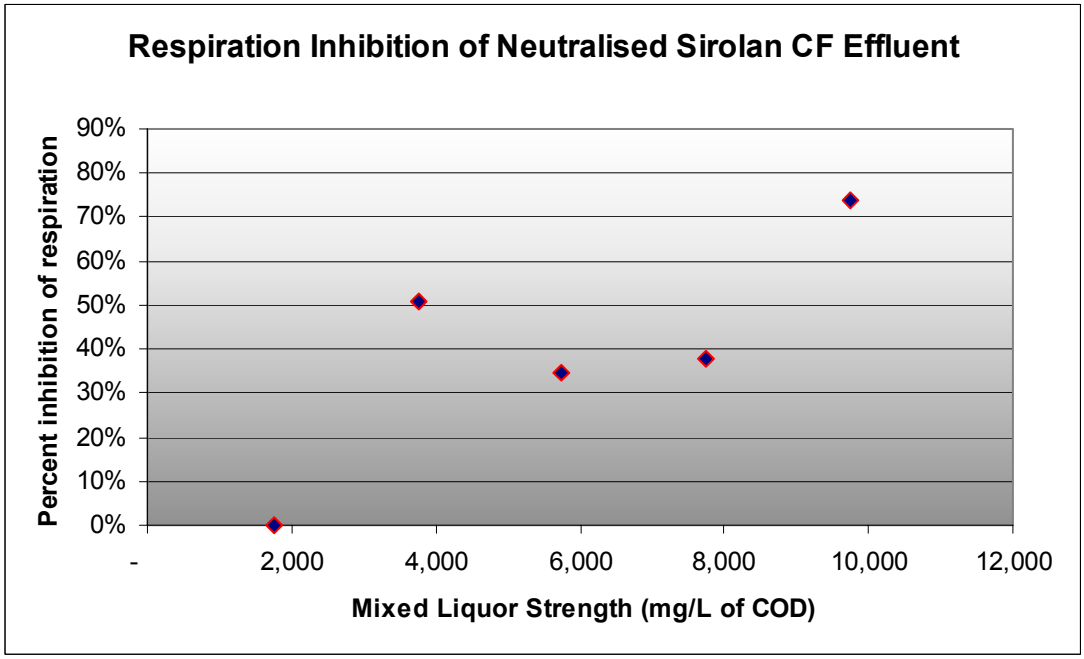


Figure 6.25 Inhibition of respiration by neutralised Sirolan CF liquor

By comparison with Figure 6.24 it can be seen that the inhibition effect displayed by the neutralised effluent in Figure 6.25, although definitely occurring, is nowhere near as clear-cut, and does not reach as high a level of inhibition as the raw acidic effluent until high substrate concentration is reached (77% inhibition at just under 10,000mg/L COD).

The unusually high level of inhibition expressed by the sample of COD = 3,750mg/L (Figure 6.25) can be partially explained by examining the time response of dissolved oxygen uptake by the biological culture exposed to each Sirolan CF feed concentration.

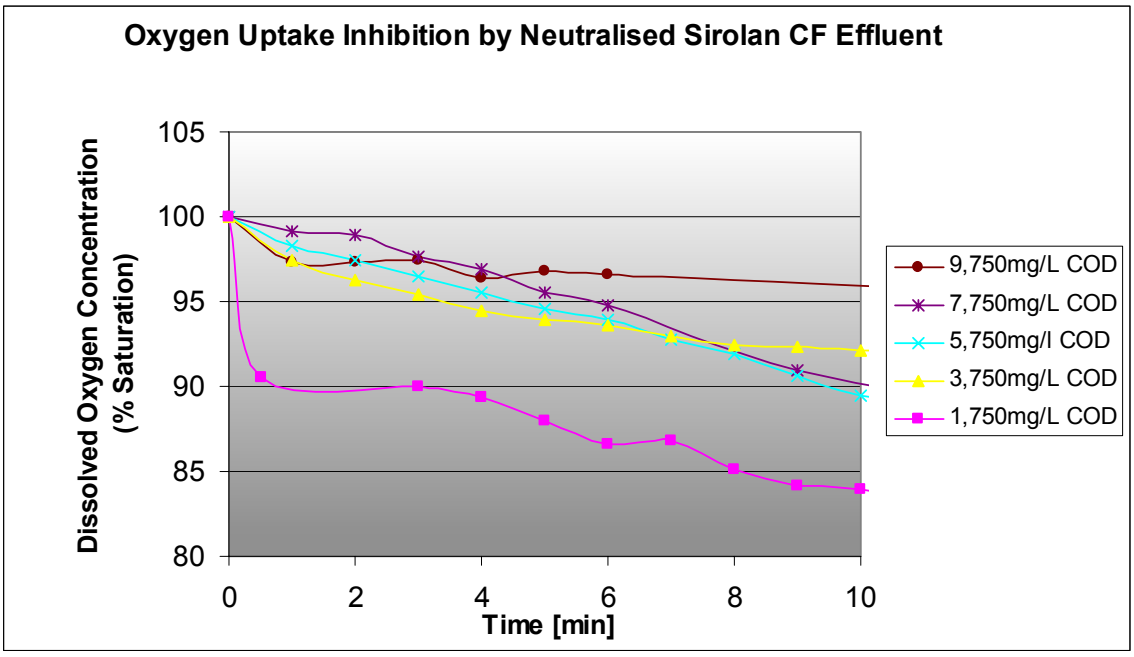


Figure 6.26 Oxygen uptake of biological culture exposed to neutralised Sirolan CF effluent

It can be seen by the yellow 3,750mg/L COD line in Figure 6.26 that although a high initial oxygen uptake rate was encountered under these conditions, this slowed after 5min of respiration resulting in a lower average oxygen uptake rate over the initial 10 minutes of exposure to the effluent sample. This slowing of oxygen uptake subsequently resulted in the higher value for maximum oxygen uptake rate inhibition expressed in Figure 6.25 for this run. If the respiration rate is taken over the first 5 minutes of each run Figure 6.25 becomes Figure 6.27:

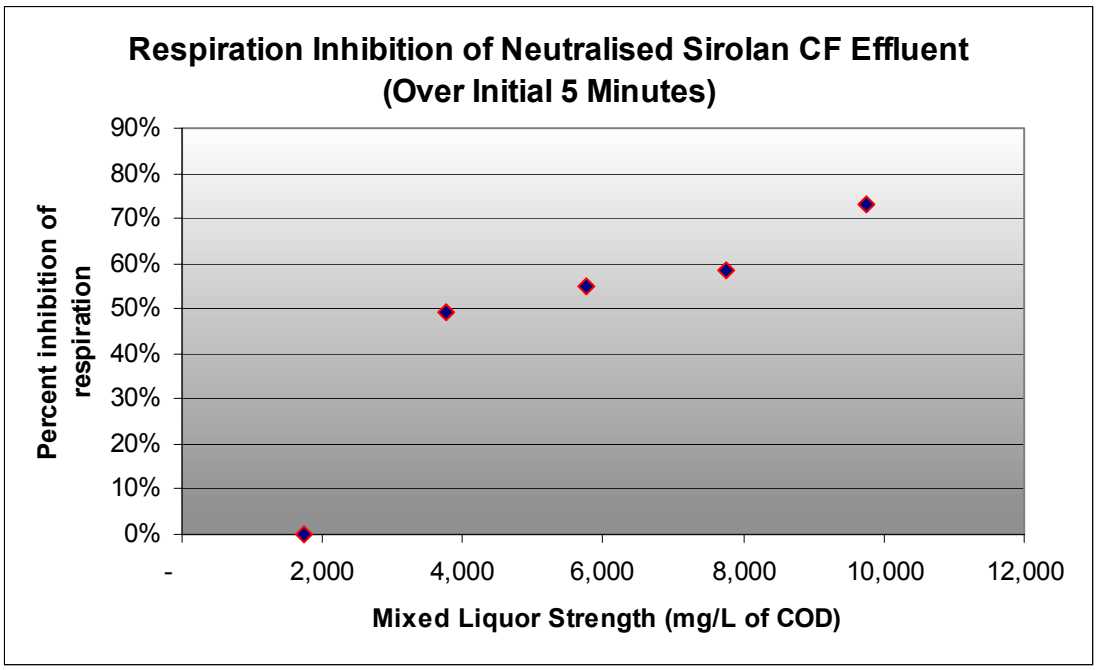


Figure 6.27 Inhibition of respiration over initial 5 minutes.

By comparison with the results yielded for inhibition of initial (10min basis) respiration rate in the low pH Sirolan CF effluent (Figure 6.24), those yielded by analysis of neutralised Sirolan CF effluent never achieved the same level of inhibition at high concentration, but did however express similar, if not more, inhibition effect at lower substrate concentrations (Figure 6.25).

6.3.3.2 Inhibition of Respiration by Low pH (Sulphuric Acid)

In order to further isolate the contribution of feed acidity to the inhibition of the activated sludge process, a third investigation was carried out into the effect of dilute sulphuric acid on respiration of the biological culture. Initially a pH response curve was developed by adding known quantities of acid to a known volume of mixed liquor. The resultant pH response curve of Sirolan CF-B liquor is shown in Figure 6.28 below:

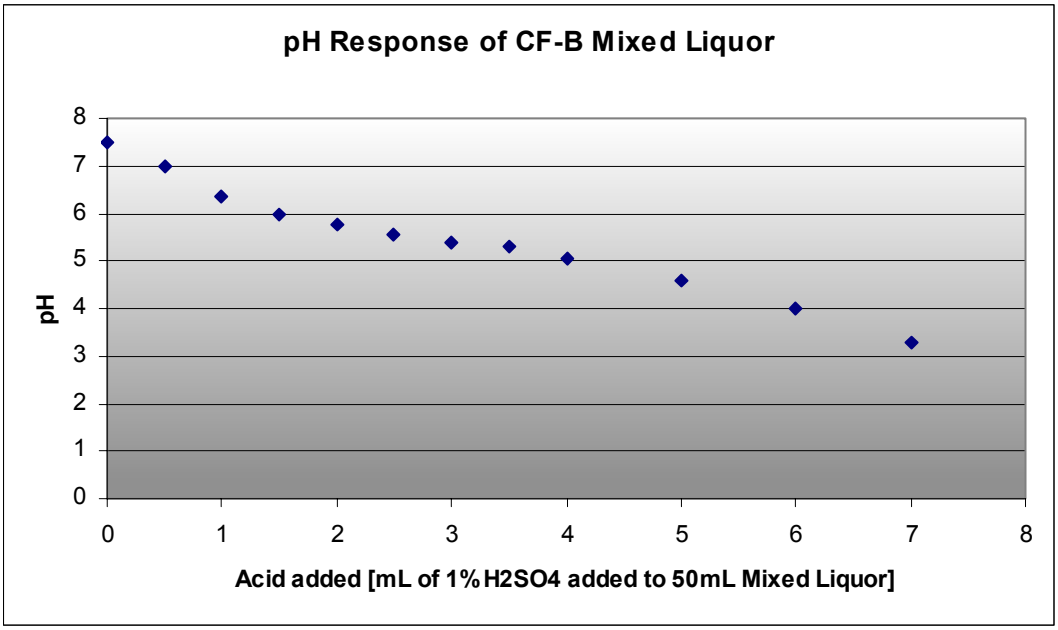


Figure 6.28 Response of 50mL of reactor mixed liquor to 1% sulphuric acid

Five identical 100mL samples of mixed liquor were then taken from an operational aerobic reactor acclimatised to a feed of pH 3 Sirolan CF Effluent. Immediately after removal from the aerobic reactor each sample had a known quantity of 1% sulphuric acid added (0, 2, 4, 6, or 8mL) and the dissolved oxygen concentration was monitored in a continuously stirred beaker (Figure 6.16). The results are expressed in Figure 6.29 and Figure 6.30 below:

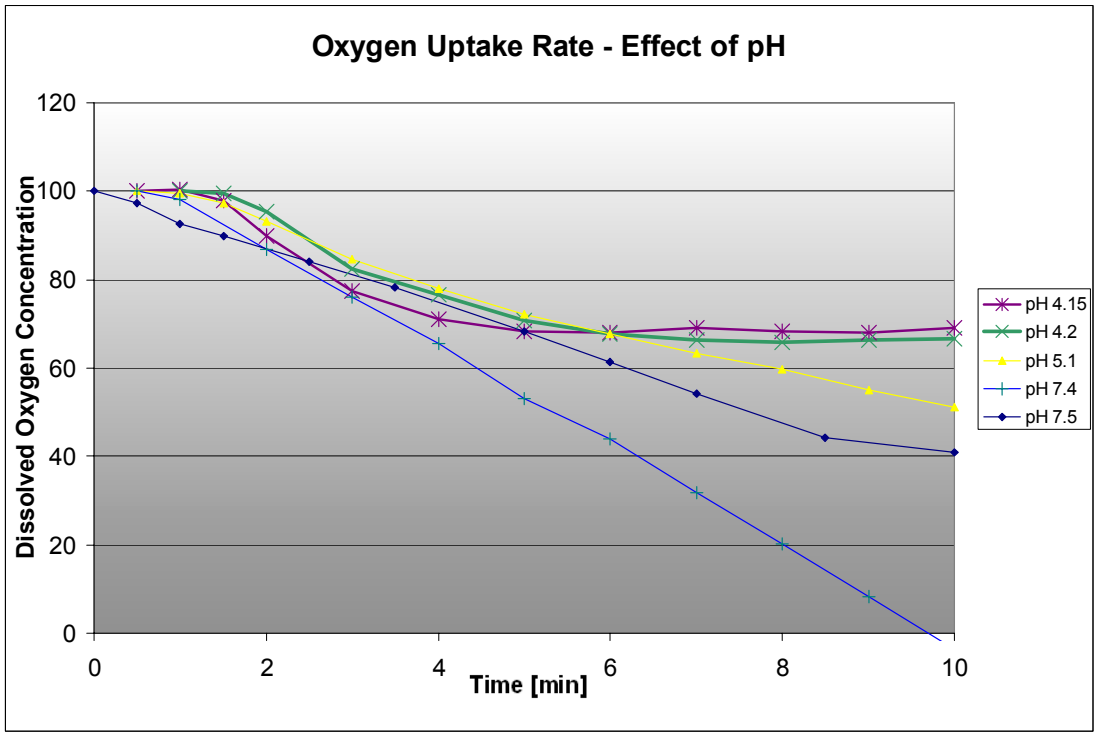


Figure 6.29 Oxygen uptake rate – effect of pH

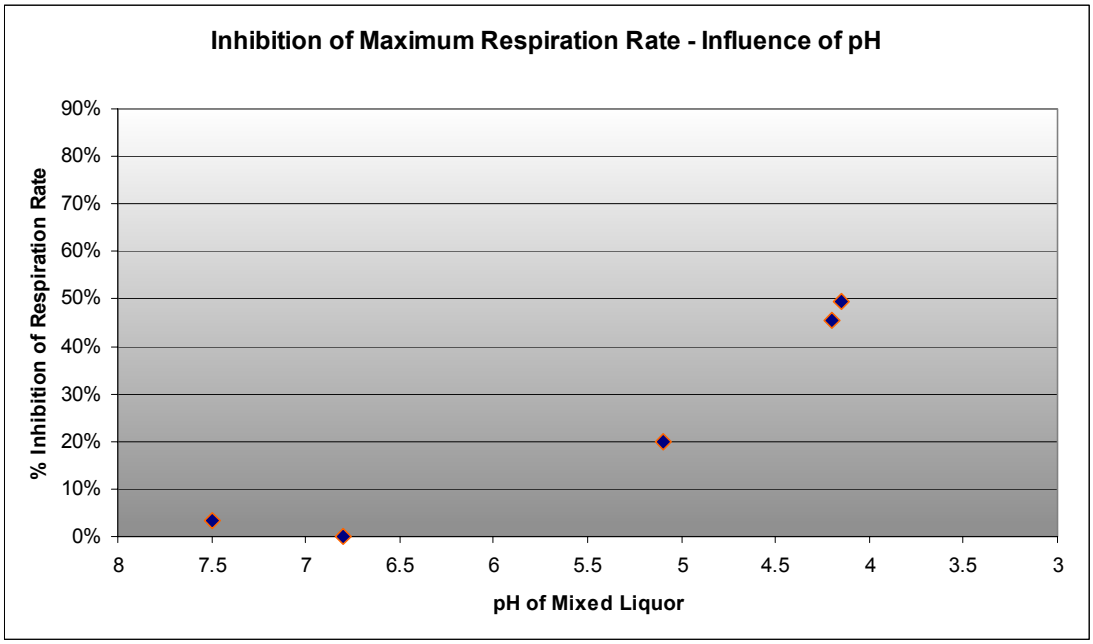


Figure 6.30 Inhibition of respiration rate of biological culture by pH

By converting the operating pH to a pseudo toxic concentration (C_{PT}) by the use of Equation (30), and using the ratio of respiration rate at a given pH to maximum respiration at pH 7 illustrated as $\frac{\hat{\mu}}{\hat{\mu}_I}$ in Equation (32) the pH inhibition Coefficient (K_I) can be determined by Lineweaver – Burke Plot (Ko *et al.* 2001) as shown in Figure 6.31:

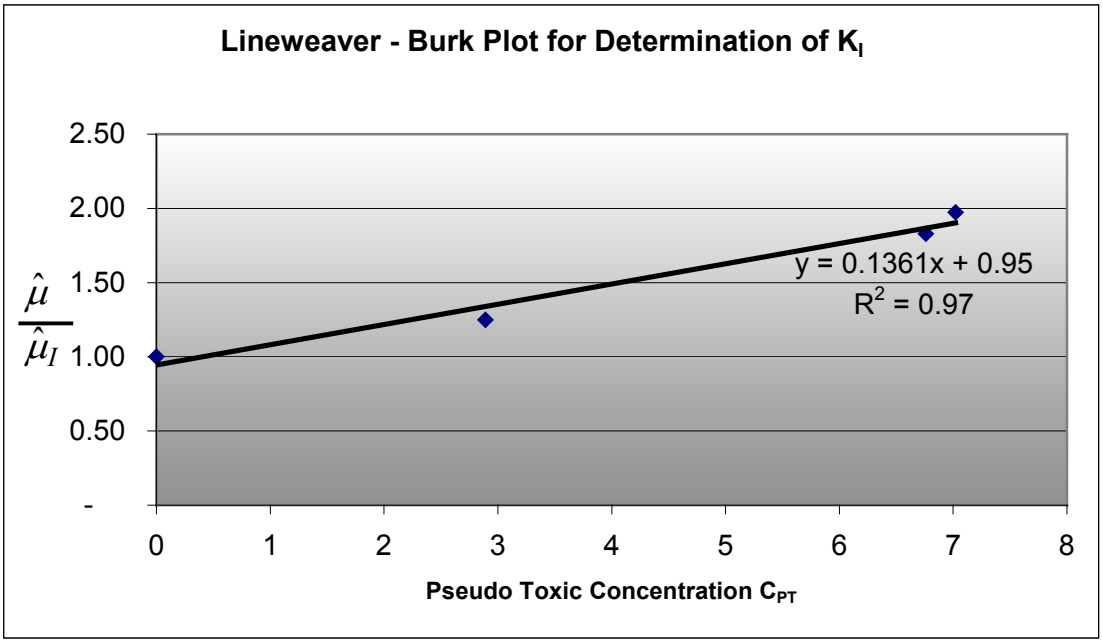


Figure 6.31 Lineweaver-Burk plot for determination of pH inhibition coefficient K_I

K_I in Equation (31) can be determined as the reciprocal slope of the straight line which intercepts the y-axis at +1.

$$\text{Therefore: } K_I = 0.1361^{-1} = 7.35$$

And Equation (31) becomes:

$$\hat{\mu}_I = \frac{\hat{\mu}}{(1 + \frac{C_{PT}}{7.35})} \quad (46)$$

6.3.4 MECHANICAL DEVICES FOR FOAM CONTROL

With regard to the rotating perforated plates tested for foam breaking properties, the best results were produced by piece (d) in Figure 6.18. This large rectangular perforated plate was closest in diameter to that of the bucket used for foam generation, and it also had the largest overall surface area. The least effective shape was the small circular piece (b. in Figure 6.18). Note that this was significantly less effective than (a) which is of similar surface area and material.

a) Prior to rotation

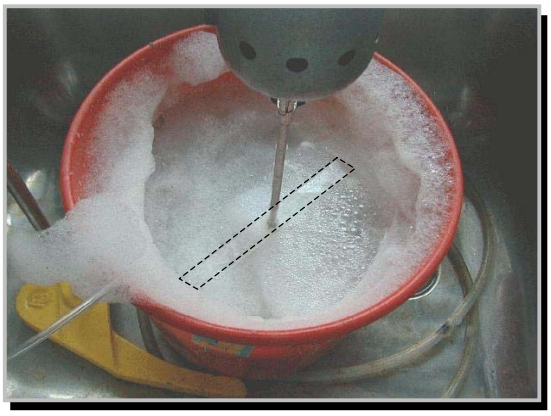
b) Rotating at low speed (50 – 80rpm)

c) Rotating at high speed (200 – 300rpm)

d) After 15min rotating at high speed

Figure 6.32 Rotating perforated sheet (d) in foam generation device

Also trialled was a thin strip of Perspex of similar length to the diameter of the foam generation device. This produced a similar result to the large perforated sheet (d in Figure 6.18) with significantly less power draw. The only drawback of this particular design was its inability to break down foam that had accumulated above the impeller before start-up (Figure 6.33 b, c).



a) Perspex blade prior to rotation

b) Perspex blade rotating slowly (50– 80 rpm) with large head of foam above blade prior to rotation

c) Perspex blade rotating at high speed (200 – 300 rpm) with large head of foam above blade prior to rotation.

d) Perspex blade rotating at high speed (200 – 300 rpm) with foam moving up through plane of rotation

Figure 6.33 Mechanical foam breaking with rotating Perspex blade

6.3.5 SLUDGE QUALITY ANALYSIS

Micrographic examination of the mixed liquor from the Bioflo 3000 reactor showed clear evidence of biomass present under all operating conditions experienced during continuous operation.

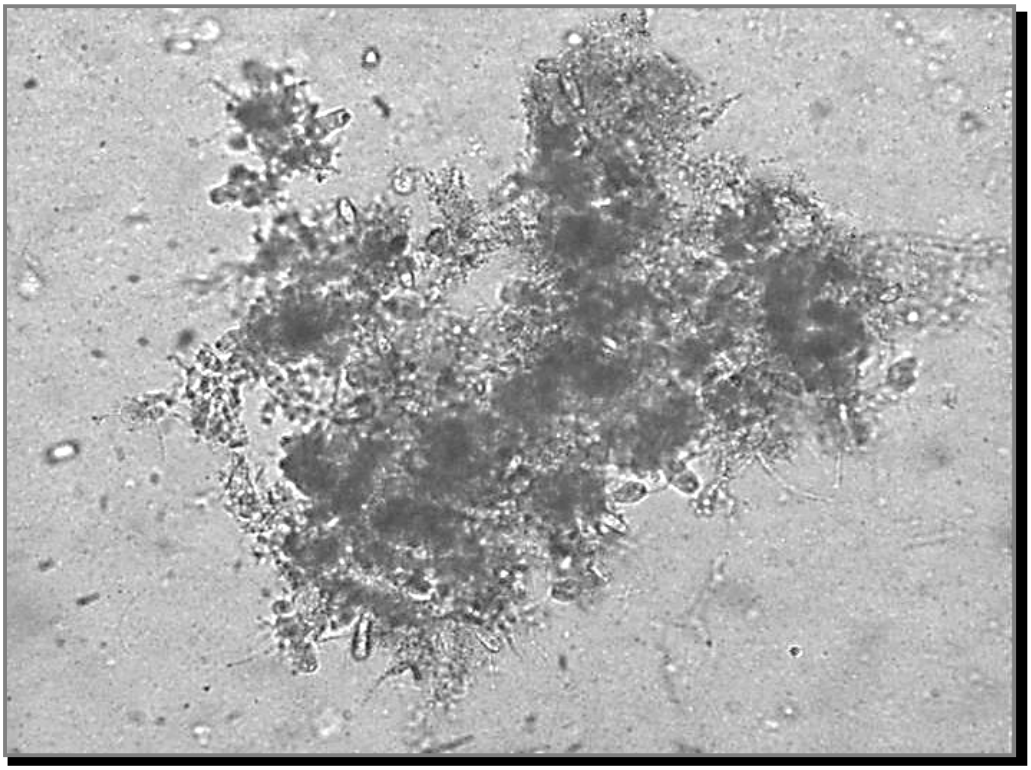


Figure 6.34 Biological floc present in 2,500mg/L MLSS mixed reactor liquor (Phase contrast, 100 x magnification)

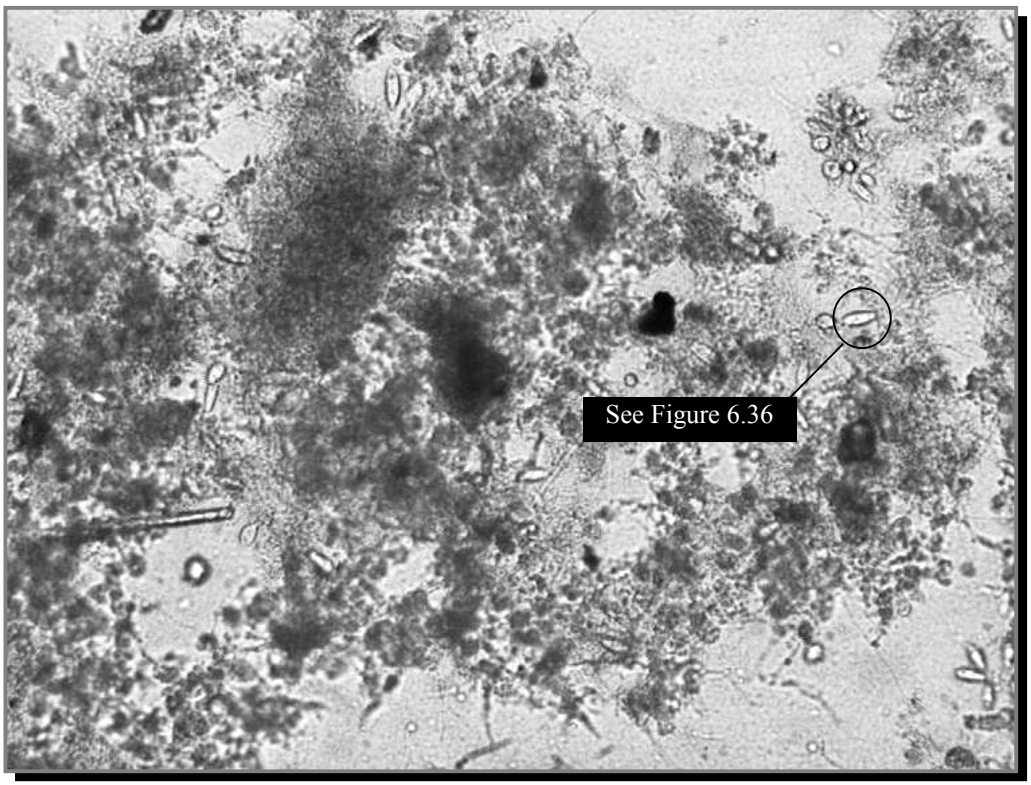


Figure 6.35 Biological flocs in 4,000mg/L MLSS mixed reactor liquor (Phase contrast, 100 x magnification)

Figure 6.36 Typical ciliated protozoa in mixed liquor samples (Phase contrast, 1000x magnification)

All of the microbial cultures observed were highly flocculated as illustrated in Figure 6.34, with a very low level of filamentous organisms present (Figure 6.35). A large number of highly motile ciliated protozoa were observed in all samples (Figure 6.36).

The large numbers of ciliated protozoa present (circled in Figure 6.35) were primarily of the type shown in Figure 6.36, and were tentatively identified as belonging to the family *Prostomatida Metacystidae* (Lee *et al.* 1985).

6.4 DISCUSSION

6.4.1 PROCESS FEASIBILITY AND OVERALL EFFECTIVENESS

The goal of the laboratory scale experiments carried out in the 5L Bioflow3000 reactor was to verify the effectiveness of a continuous mix aerobic activated sludge process biologically treating acidic wool scouring effluent pre-treated by the Sirolan CF chemical flocculation process. This investigation was also aimed at collecting sufficient rate data to develop a kinetic model of the reactions involved.

Initial work at a hydraulic residence time of 36 hours in the aerobic reactor revealed unstable behaviour with a high requirement for pH neutralisation by addition of supplementary sodium hydroxide solution. The inability of the biological system to effectively degrade the organic material in the effluent at short residence times confirms that this effluent should not be classified as "readily biodegradable". This is contrary to laboratory scale results provided by the CSIRO, which suggest that no more than 24 hours hydraulic residence time is required for an aerobic system treating Sirolan CF liquor (Poole *et al.* 1999). Although Poole *et al* found that only four hours hydraulic residence time were required to obtain 90% BOD_5 removal in the laboratory scale continuous reactor with supplemental pH neutralisation, pilot scale studies by the same author showed that at least 48 hours residence time was required to achieve this level of treatment. This later finding is consistent with results published by Bateup (Bateup *et al.* 1996), which report 31 hour and 97 hour hydraulic residence times giving 88% and 97% BOD_5 removal respectively in a 3,000L pilot plant. Both Bateup *et al* and Poole *et al* processed Sirolan CF liquor obtained from an Australian wool scour. This effluent was approximately one third the strength of typical Sirolan CF effluent produced from a New Zealand Scour (Table 6.10).

Table 6.10 Typical effluent strength used in aerobic biodegradation experiments [a](Poole *et al.* 1999)

Component [mg/L]	CSIRO Test Conditions[a]	Equivalent New Zealand Condition
Raw Scour Effluent COD	45,000	100,000
Raw Scour Effluent BOD_5	17,500	35,000
COD after Sirolan CF	5,750	27,000
BOD_5 after Sirolan CF	1,650	7,500
SS after Sirolan CF	180	600

The difference in effluent strength found between New Zealand wool scours typically processing crossbred fleece wools and Australian wool scours processing almost entirely merino wool can be primarily attributed to a dilution factor. The New Zealand Scours investigated typically use 1.0 – 2.0 litres of wash water per kg of greasy wool processed, whereas Australian scourers often utilise 4 .0 – 5.0 litres of wash water per kg of greasy wool. The subsequent dilution of the effluent produced results in the reduced concentration of contaminants in the Australian effluents (evident in Table 5.2, Table 6.8, and Table 6.10)

When a hydraulic residence time of 50 hours was utilised in the laboratory scale bioreactor, results similar to those obtained in the CSIRO's pilot plant studies were observed. At this feed rate, stable operation was achieved with minimal base addition required at feed concentrations of up to 7,000mg/L BOD_5. At start-up, and under high BOD_5 loading rates (over 7,000mg/L BOD_5) periodic addition of 10% caustic soda was required to maintain operating pH > 6.5, but the reactor otherwise operated stably at pH 8.0 ± 0.2, without the requirement for automated pH control. This self neutralisation property of the biological process alone is capable of saving a scour already operating the Sirolan CF pre-treatment process approximately NZ$245,000 per year in caustic soda if they are currently required to neutralise their effluent to pH > 6.0 prior to discharge (based on Orica Chemnet, Bulk 50% Caustic Soda *Liq*. at NZ$1.00/L, for delivery to Christchurch, NZ, 18 September 2002 – spot price of caustic soda will vary significantly with time and location)

When the pH did begin to drop due to overloading of the reactor, failure to maintain the pH > 6.5 by supplementary caustic soda addition led to a continued drop in pH of the reactor to that of the feed (pH 3.3 – 4.3) and subsequent death of the microbial culture.

This can be explained by the pH inhibition results illustrated in Section 6.3.3. Figure 6.30 shows that at normal operating pH of 6.5 – 8.0 there is minimal inhibition of respiration occurring due to pH. Under normal operating conditions the pH of the reactor is maintained by production of pH buffering metabolites by the biological culture combined with CO_2 evolution and stripping (Male *et al.* 2001). It must therefore be recognised that the pH operating point is an inherently unstable one, and any deviation downwards in pH will therefore be self-perpetuating. For example: if the pH of the reactor drops to 5.5, there will be an approximately 10% decrease in the growth rate of the biological culture (Figure 6.30). One consequence of this decline is a reduced quantity of pH buffering by the micro-organisms, which if not rectified (e.g. by addition of caustic soda to the reactor basin) will lead to a further decrease of pH, and so on until the reactor is no longer able to sustain the required biological culture.

In Table 6.9 (page 110), which illustrates the results of the Bioflo3000 aerobic activated sludge process, two results stand out as having significantly higher product BOD_5 than the mean of 350mg/L. These results of 1,200, and 1,100mg/L residual BOD_5 in the reactor product were both obtained immediately after a restart of the continuous reactor and significant pH problems were encountered during both of these runs, requiring intermittent caustic soda dosing to maintain pH > 6.5. Disregarding these two runs, the average residual BOD_5 and % BOD_5 removal in the laboratory scale reactor was 253mg/L BOD_5 and 93% respectively.

As is often presented as the case with biological treatment systems (Adams *et al.* 1975; Grady *et al.* 1975; Eckenfelder 1992; Orhon *et al.* 1994; Orhon *et al.* 1999; Cicek *et al.* 2001) the residual BOD_5 in the effluent of the Bioflo3000 reactor is, to a certain extent, independent of the BOD_5 concentration in the feed influent (Figure 6.37). Rather, as the BOD_5 concentration of the feed to the reactor increases, the level of biomass also increases to maintain a more or less constant effluent BOD_5 (Figure 6.38)

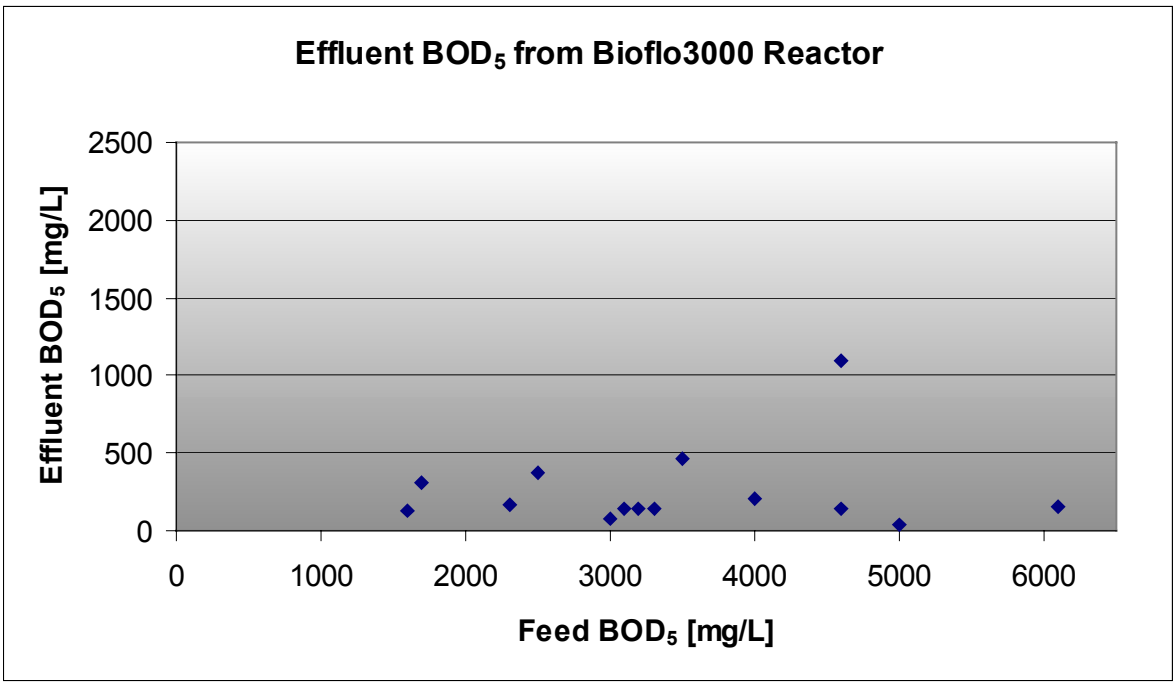


Figure 6.37 Effluent BOD_5 from the Biolo3000 laboratory reactor

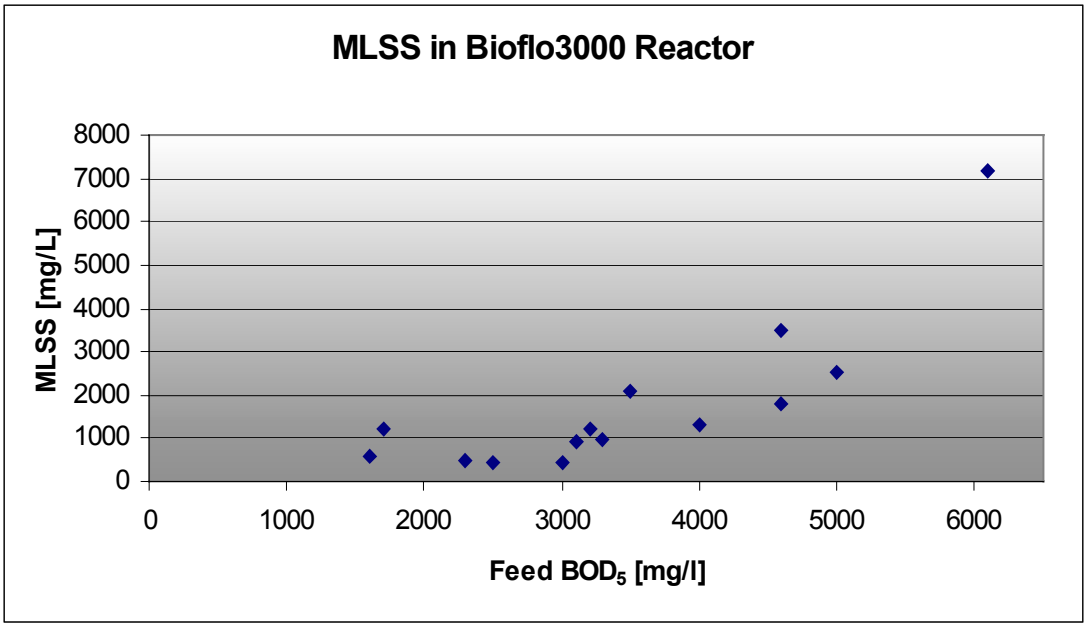


Figure 6.38 MLSS in the Bioflo3000 reactor

6.4.2 KINETIC MODELLING

Both the initial feasibility experiments (Figure 6.22, page 140) and the respirometry investigation (Figure 6.23 and Figure 6.24, page 141) indicated that the biological system did not follow standard Monod style biological kinetics as given by Equation (18), but rather some form of inhibition of microbial substrate uptake was occurring at high organic loading rates.

All kinetic investigations were carried out using the bulk effluent quality parameter BOD_5 to represent the substrate concentration. The aim of this was to keep the information collected about the process as relevant as possible to that which is used in the operation and control of industrial effluent treatment plants. Also, the overall goal of the proposed biological treatment plant is to remove the biodegradable organic contamination measured as BOD_5 from the pre-treated wool scouring effluent. Thus, as BOD_5 is the parameter by which performance of the process is evaluated, it is the obvious choice of parameter for quantifying the rate kinetics that will be used in the design of an industrial scale plant.

The occurrence of substrate inhibition was verified by respirometric analysis of the response of an acclimatised mixed culture to varying concentrations of the feed liquor (Section 6.3.2). In these investigations the trials at different substrate concentrations were carried out consecutively, but in random order to eliminate any trend introduced by possible drift of the

dissolved oxygen probe used. The results of this investigation showed a clear trend towards a reduction of maximum respiration rate at increased substrate concentrations (Figure 6.23, Figure 6.24). When modelling biological kinetics, the Haldane model of substrate inhibition (Equation 22) is traditionally applied in cases where the substrate is observed to be inhibitory (Atkison *et al.* 1991). In this case however the Haldane model, which is derived from enzyme kinetic theory was found to be unable to predict the substrate uptake rate under the range of operating conditions encountered in this investigation (Figure 6.39).

The model curve in Figure 6.39 was generated by fitting the Haldane kinetic model given above as Equation (22) to the experimental data. The parameters K_S, and K_{IS} were determined by minimisation of the sum of squares of the regression between the predicted and observed growth rates by the Newton method (as applied via the Solver function of Microsoft Excel).

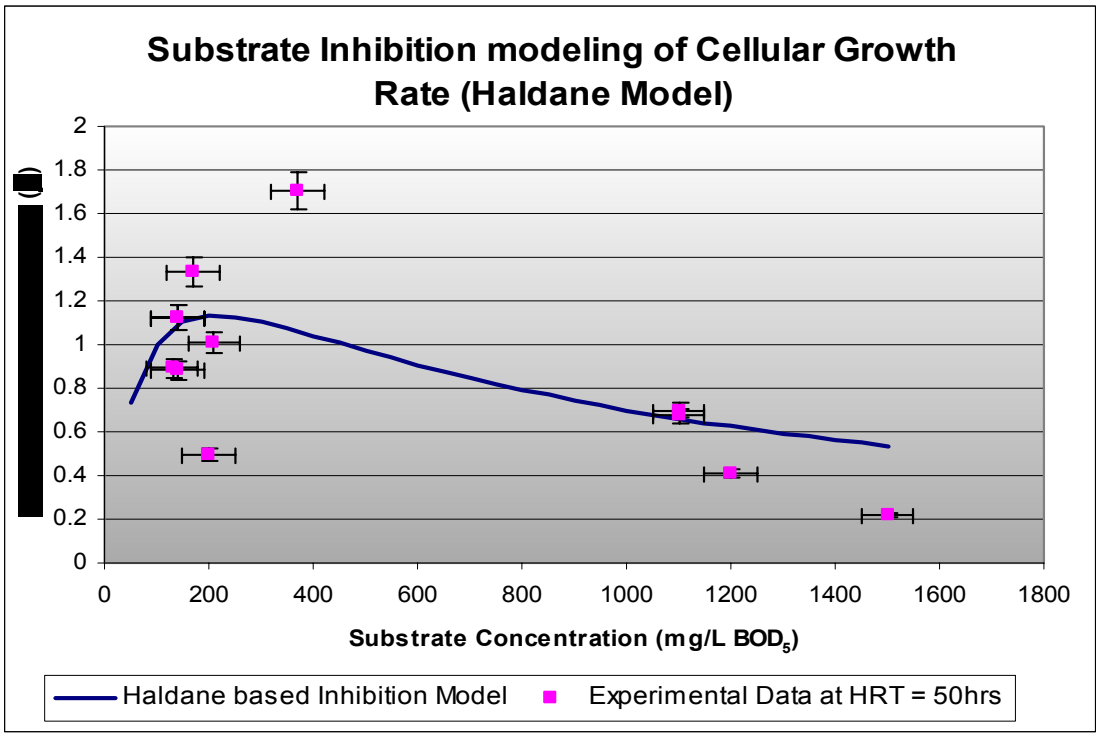


Figure 6.39 Haldane modal of substration inhibition vs experimental data collected at HRT of 50hrs

The substrate inhibition models represented by Equations (24) to (28) proved similarly ineffective at modelling the substrate uptake and cellular growth observed under experimental conditions (results presented in APPENDIX I). Equation (29) proposed by Wayman and Tseng (Wayman *et al.* 1976) however very closely modelled the results obtained under experimental conditions using a continuous flow reactor of 50 hour hydraulic residence time. It can be seen from Figure 6.39 and Figure 6.40 that there is a lack of data points present in

the experimental data in the range of 500 – 1,000mg/L BOD_5. This was attributed to the inhibition which begins to occur at mixed liquor substrate concentrations of BOD_5 > 500mg/L reducing the product quality so that residual BOD_5 of less than 1,000mg/L could not be achieved by the 50hour residence time reactor once the mixed liquor concentration exceeded this level. Although the discontinuity of the model at the threshold substrate concentration S* is considered a significant drawback in the use of this model, its prediction of a maximum substrate concentration at which all growth stops is an advantage over other Haldane style relationships (Luong 1987; Meric *et al.* 2002).

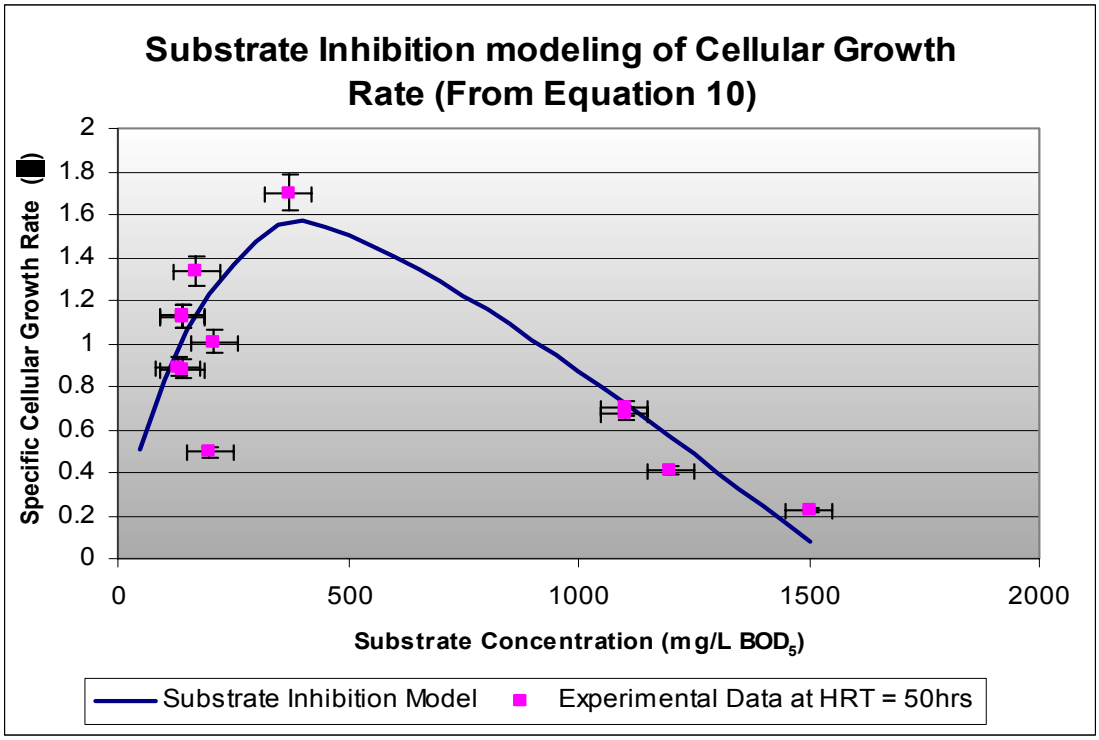


Figure 6.40 Substrate inhibition of cellular growth rate

As a range of concentrations of raw acidic effluent was used in the substrate inhibition investigation (Section 6.3.2), an increase in substrate concentration would have resulted in a concomitant decrease in pH of the mixture. In order to isolate the effect of this reduced pH on respiration rate as measured in the substrate inhibition tests, the test was repeated with the same raw feed effluent, this time neutralised to pH 7.0 prior to being added to the respirometer. By comparing Figure 6.27 with Figure 6.24 (pages 144 and 142 respectively) it can be seen that the inhibition of maximum respiration rate occurring at high substrate concentration (>6,000mg/L COD) is reduced by approximately 8 – 15% by neutralising the feed effluent.

Finally, in order to clearly identify the level of inhibition occurring due to low pH, a mixed biological culture that had been acclimatised to Sirolan CF effluent at pH 3.5 was exposed to a range of pH conditions by the addition of dilute sulphuric acid (the same acid as used to achieve low pH in the Sirolan CF pre-treatment process) to the respirometry cell. The results of this respirometric evaluation of pH inhibition (presented in Section 6.3.3) confirm that the biological system closely followed non-competitive pH inhibition kinetics as detailed in Section 6.1.1. A Lineweaver-Burk Plot of maximum growth rate reduction (measured as suppression of respiration rate) versus pseudo toxic concentration C_{PT} (Figure 6.31 on page 146) proved to be linear ($r^2 = 0.97$) with a y-intercept of 0.95. This corresponds well with the result predicted by Equation (32) for non-competitive inhibition kinetics. Equation (32) predicts a linear relation between $\frac{\hat{\mu}}{\hat{\mu}_I}$ and C_{PT} with a y-intercept of +1 if non-competitive inhibition kinetics are followed.

Thus the kinetic model for combined substrate and pH inhibition becomes:

$$\left.\begin{aligned} \mu_{IS} &= \frac{\hat{\mu}_I S}{K_s + S} \quad when \quad S < S^* \\ \mu_{IS} &= \frac{\hat{\mu}_I S}{K_s + S} - K_{IS}(S - S^*) \quad when \quad S > S^* \end{aligned}\right\} \qquad (29)$$

Where:

$$\hat{\mu}_I = \frac{\hat{\mu}}{(C_{PT} + \frac{C_{PT}}{K_I})} \qquad (31)$$

$$C_{PT} = \left(pH_{th} - pH_r\right)^2 \qquad (30)$$

And for an aerobic reactor processing acidic Sirolan CF effluent:

$\hat{\mu}$ = 2.4 [d^{-1}]

K_S = 187 [mg/L]

K_{IS} = 1.81 x 10^{-3}[mg/L]

S^* = 400 [mg/L BOD_5]

K_I = 7.35

pH_{th}= pH 6.5 for acidic conditions

= pH 8.0 for basic conditions

In circumstances where the feed to the reactor was maintained at a BOD_5 of less than 4,000mg/L (Figure 6.21), and a hydraulic residence time of at least 50 hours, the system was observed to be self-neutralising and operated stably at a pH of 7.5 – 8.5 despite the high acidity (pH 3.0 – 4.0) of the feed. Therefore, if these feed conditions were maintained, the pH inhibition kinetics described here would only take effect during transient shock loading and at start-up when the mixed culture is insufficiently acclimatised to provide pH buffering.

A key point where the results of pH inhibition testing become useful in the design process is where aerobic, anoxic, and contact stabilisation selector zones are to be used prior to the main aerobic digester. In these zones the return activated sludge is brought into contact with a high concentration of the acidic feed effluent. In the case of the low pH feed from the Sirolan CF process, this concentrated feed must be diluted with mixed liquor from the main reactor vessel (See Figure 9.3, page 213) to ensure an acceptable level of pH is maintained in the selector vessel. The inhibition of biological activity due to pH, illustrated in Figure 6.30, provides an excellent tool to aid in the determination of what the minimum pH of the selector vessel should set to. From this figure we can conclude that any pH below 5.0 ~ 5.5 will significantly inhibit biological activity in the selector vessel. While taking this approach it must be noted that other factors also influence the pH range required in the selector vessel. If denitrification is desired then the pH of the anoxic zone in which denitrification is occurring should be maintained at a level close to 7.0. Randall (Randall *et al.* 1992) summarises work from a range of investigations which all report that the denitrification rate is optimal between pH 7 – 8, and decreases linearly from pH 7 – 4 (Wiljer *et al.* 1954; Nommik 1956; Bremner *et al.* 1958). Similarly, the purpose of a selector vessel is primarily selection of bacteria with superior settling characteristics by introduction of a substrate gradient to the reactor system. The high substrate concentration in the feed vessel promotes the growth of flocculating bacteria over filamentous organisms that proliferate under diffusion-limiting conditions. Low pH hinders this process by favouring growth of filamentous fungal biomass, which also has poor settling characteristics (Zeikus *et al.* 1991; Randall *et al.* 1992).

6.4.3 MECHANICAL DEVICES FOR FOAM CONTROL

Of all the rotating blades tested for their foam breaking capabilities the best results were obtained by those items possessing the following properties:

1. Large diameter such that only a small quantity of foam was able to flow up around the rotating blade.

2. The ability to impart both impact force and shear force upon the foam passing through the plane of rotation.

The least effective geometry used, a circular sheet of perforated plate of diameter significantly smaller than the vessel in which the foam was being generated, exhibited neither of these properties, while the most effective shapes exhibited both of these properties.

Test pieces that imparted a strong impact force on the foam, such as the thin Perspex blade, were most effective in destroying foam passing up through the plane of rotation. Test pieces that imparted a high shear force on the foam however, such as the large surface area rectangular perforated plate, were more effective at destroying foam that had accumulated above the plane of rotation.

The most significant problem with using a rotating foam breaker in the headspace of the digester tank is the health and safety aspect of having a large blade rotating at high speed in an environment where plant operators can potentially come into contact with it. This would be particularly relevant in cases where the foam level did exceed the height of the blade, as the rotating blade would then be concealed in the foam, increasing the chance of operators accidentally coming in to contact with it.

A practical alternative would be to have the rotating foam breaker housed in a separate vessel into which the foam is ducted. The condensed foam could then be pumped in as a sludge to the gravity clarifier for disposal or recycle with the rest of the overflow from the reactor vessels. This concept would also make the design of the foam handling device independent of digester tank geometry, allowing for the use of rectangular or circular tanks with open or closed tops, depending on the economics of each particular site.

6.4.4 BIOLOGICAL SLUDGE QUALITY

Micrographic analysis of the microbial population of the activated sludge in the mixed liquor of the bench top reactor showed a consistently high quality of sludge under all operating conditions investigated. The large population of ciliated protozoa present is generally considered representative of a healthy activated sludge microbial population (McCracken *et al.* 1980). Comparison of Figure 6.34 and Figure 6.35 (page 149) with Figure 6.12 (page 119) shows that the biomass samples examined by microscope contained only a very limited number of filamentous organisms. Based on Eckenfelder's quantitative filamentous bulking scale (Table 6.3, page 120) the sludge found in this system can be categorised as containing 'few' filamentous organisms. This leads to the prediction that there is very low likelihood of filamentous bulking occurring in a full-scale system operating under similar conditions as the laboratory unit. This is supported by the tendency of biomass in the laboratory reactor to form large, rapidly settling flocs, one of which is pictured in Figure 6.34.

7 5,000L PILOT PLANT STUDIES

7.1 INTRODUCTION

After initial feasibility studies had been carried out, a 5,000L continuous flow reactor was designed, built and installed at Fairlie Wool Scour Timaru Ltd. The 5,000L reactor was also set up in the configuration shown in Figure 6.1 on page 98, with the feed and sludge recycle streams being pumped and all other flows operating by gravity overflow. For this reactor, batches of feed were made up daily by processing the wool scour's heavy flow-down effluent in the pilot plant Sirolan CF pre-treatment system described in Section 5.2.1 and storing it in a 5,000L feed storage tank (Figure 7.2). Feed liquor could then be pumped continuously from the feed storage tank to the reactor vessel at a constant rate. This 5,000L reactor was operated continuously for several months, during which time the effect of process variations such as feed flow rate and strength were evaluated.

As the main operational parameters and reaction kinetics had been identified and quantified at laboratory scale, the primary purpose of the pilot plant investigation was to confirm the relevance of the laboratory results to field conditions. Performing pilot scale investigations at an operational wool scour also provided the opportunity to evaluate the effect of industrial process conditions and subsequent feed fluctuations on the effectiveness of the process.

Fairlie Wool Scour is a local wool scouring plant in Timaru installed by the Mentec Company, since amalgamated with Annett and Darling Ltd. to form ADM Group Ltd. Due to its close proximity to the ADM Group premises, this wool scour has historically been used as a test bed for emerging technology. The staff and management at Fairlie Wool Scour gave extensive assistance and full co-operation with the development of the new effluent treatment system detailed herein.

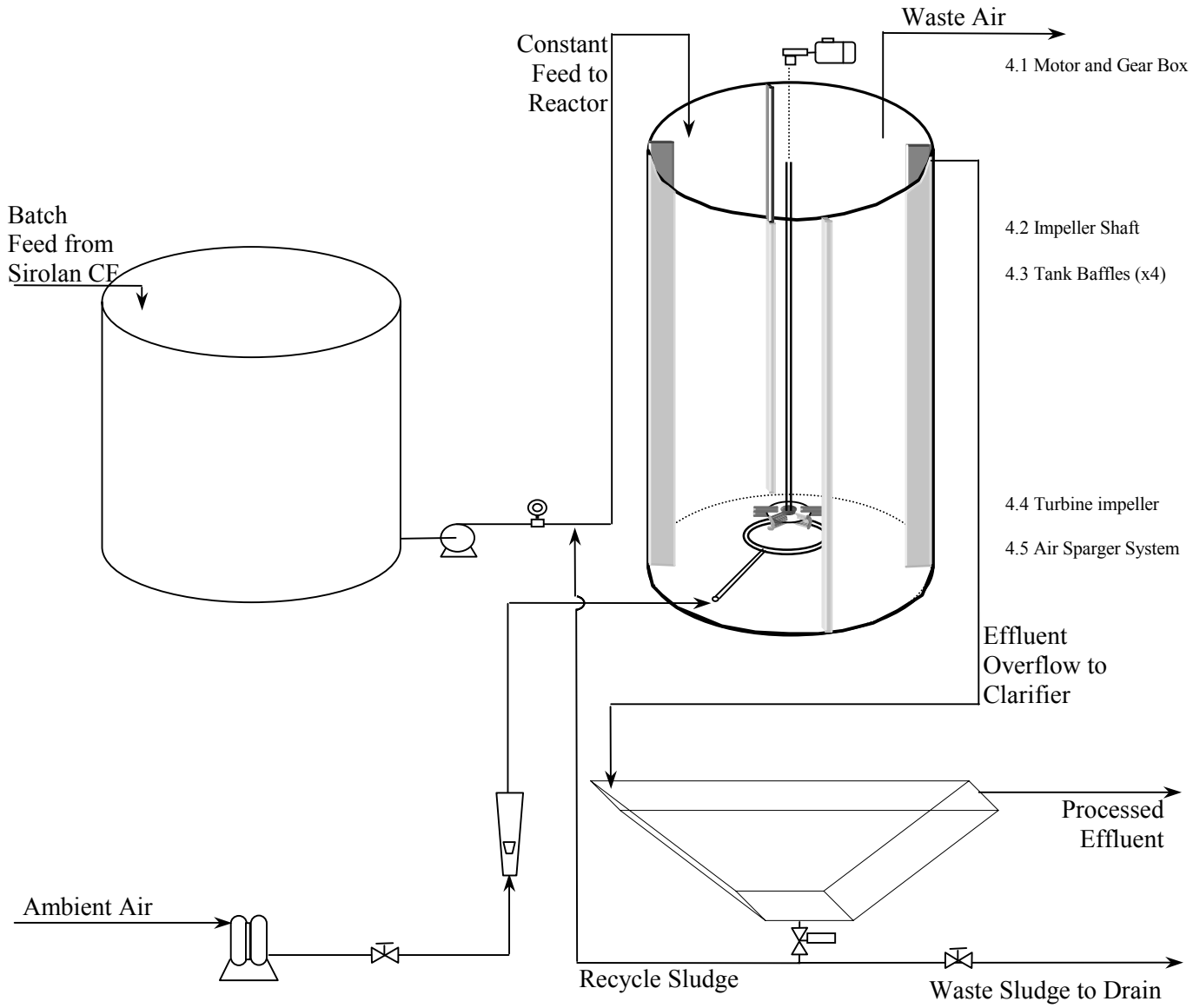
1. 5,000L aerated reactor vessel
2. Settling vessel
3. 5,000L feed storage tank
4. Decanter centrifuge of Sirolan CF Plant

Figure 7.1 5,000 litre activated sludge plant being installed at Fairlie Wool Scour

The aim of the pilot plant investigation was to evaluate the effects of scale-up on the effectiveness and robustness of the biological process. As the process was operating in a continuous manner at an operational wool scour, the effect of feed strength variation and intermittent feeding were also investigated.

7.2 EXPERIMENTAL APPARATUS

1. Feed Storage Tank
2. Effluent Feed Pump
3. Flow Meter
4. Biological Reactor Tank



5. Air Blower
6. Rotameter
7. Settling Tank

Figure 7.2 Layout of 5,000L pilot plant

7.2.1 PILOT PLANT DESIGN AND CONSTRUCTION

Figure 7.3 Hopper-bottomed vessel used as settling tank for pilot plant

The 5,000L plant was constructed primarily from materials found in storage at ANDAR's Seadown premises in Timaru. The reactor tank used was a skid mounted stainless steel open topped vessel 3,000mm tall by 1,600mm diameter (Figure 7.4).

Figure 7.4 Tank used as 5,000L reactor vessel

The two other vessels required were a settling tank and a feed storage tank. For the former, the obsolete hopper-bottomed wool scour squeeze press bowl shown in Figure 7.3 was used. The only vessel available for a feed storage tank was the 5,000L closed mild steel vessel shown on the right hand side of Figure 7.5, which was also found in storage on ANDAR premises. Although this tank was smaller than desired, meaning that feedstock would need to be made up on an almost daily basis, it was all that was available under budget constraints at the time.

Figure 7.5 Reactor tank (L) and 5,000L mild steel feed storage tank (R)

While little modification of the mild steel feed storage tank was required, the settling vessel and reactor tank both required extensive design modifications and fitting out for their specialised purposes. The settling tank required installation of feed distribution baffles, an outlet weir, and a Stamford baffle to prevent underflow short-circuiting (Figure 7.6). In addition to this, a pneumatically actuated knife-gate valve controlled by a solenoid timer was installed on the bottom of the hopper to provide periodic discharge of accumulated solids to drain.

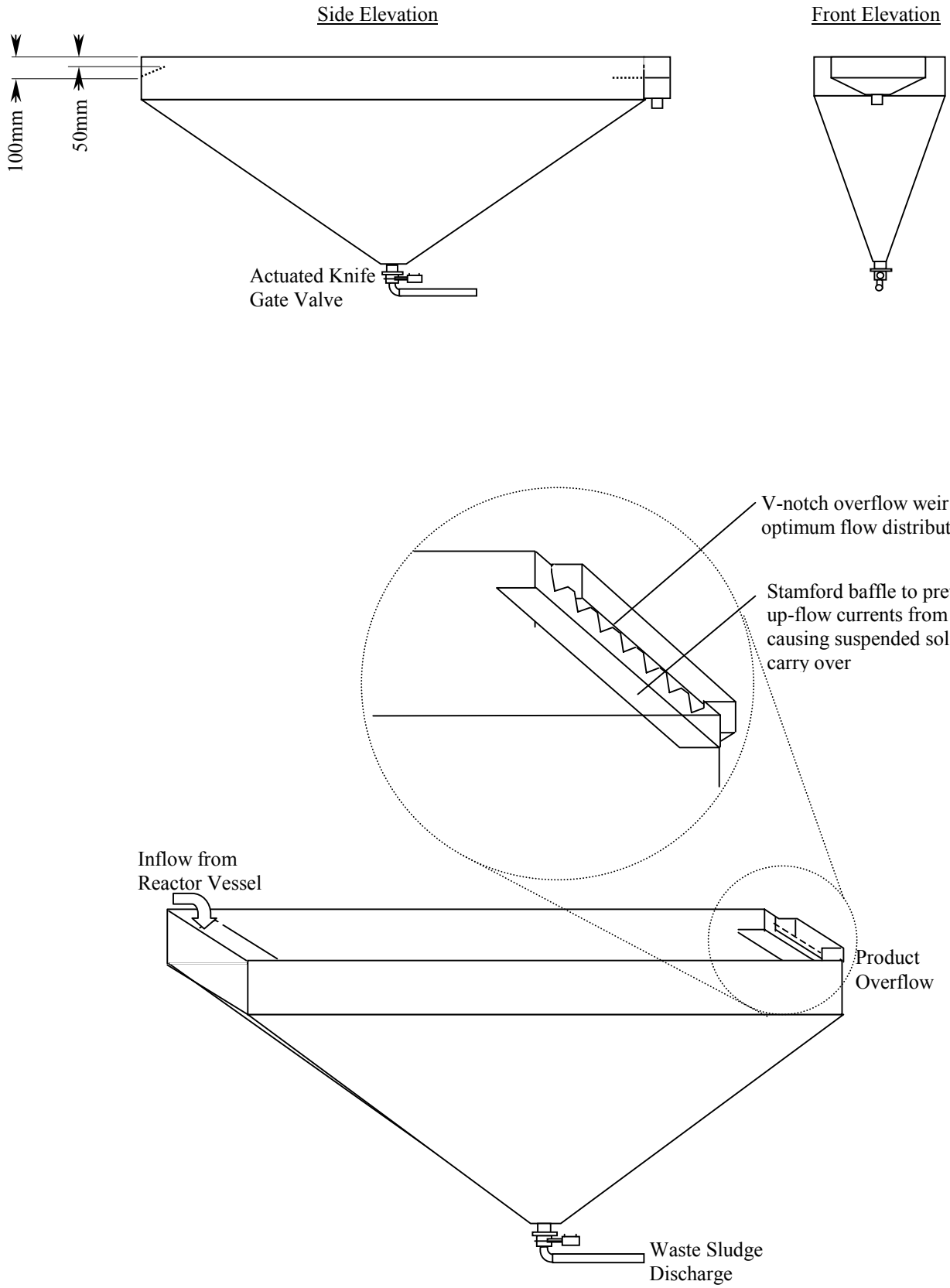


Figure 7.6 Modifications made to pilot plant settling vessel

The stainless steel vessel to be used as the aerobic reactor tank required the most design and refitting work. Oxygen demand of the reactor was determined by assuming complete removal

of the maximum COD loading to be expected. A roots blower and gas distribution impeller were then sized to fulfil this oxygen requirement.

The gas dispersion impeller used was a purpose-built six-bladed concave disc turbine as pictured in Figure 7.7.

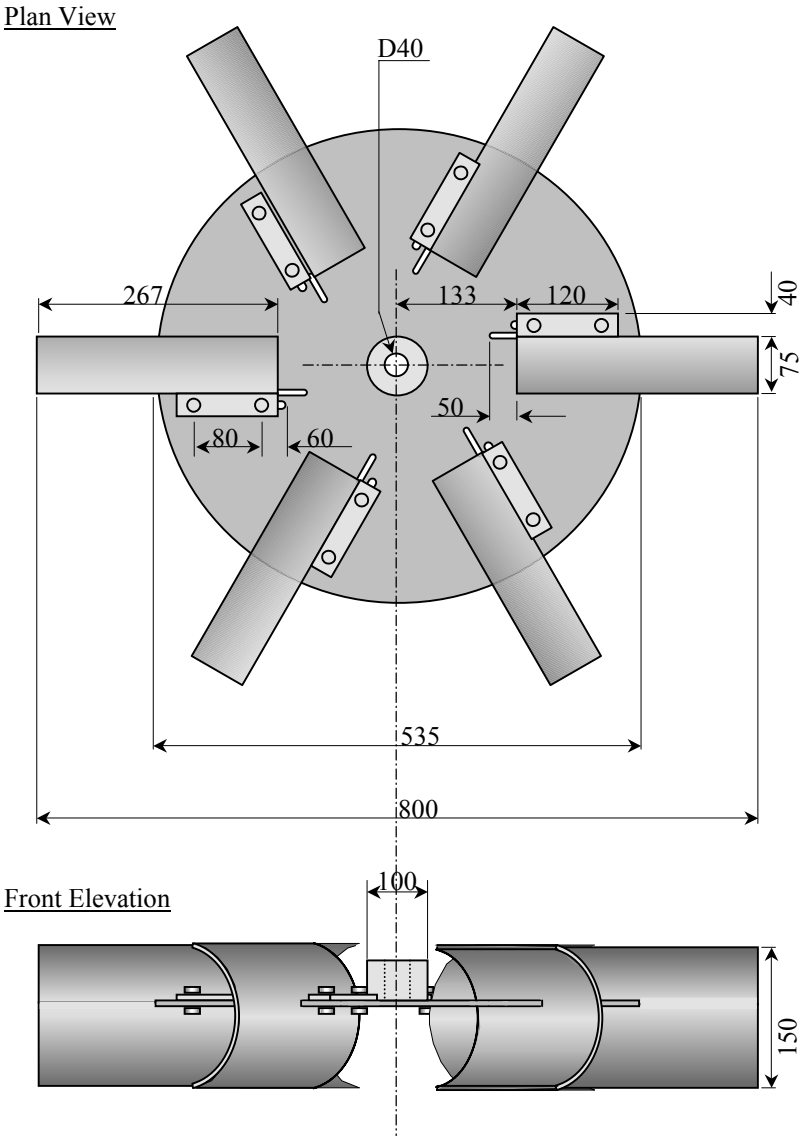


Figure 7.7 CD-6 Turbine designed and built for pilot plant aerobic reactor (all dimensions in mm)

The turbine was designed with concave blades mounted on a gas distribution disc to maximize gas distribution efficiency while minimising shear damage to the biological flocs growing in the tank (Bakker *et al.* 1994; Rutland *et al.* 1997). The impeller also utilised adjustable blade positions so that the power draw, balance and gas distribution capacity of the impeller could be adjusted during use if required. The blower used was oversized and the airflow throttled to a measured value by use of a needle valve in the air feed line. Four evenly

spaced vertical baffles were also installed in the tank to ensure axial mixing. One of these baffles can be seen in the top right hand corner of Figure 7.9 on the next page.

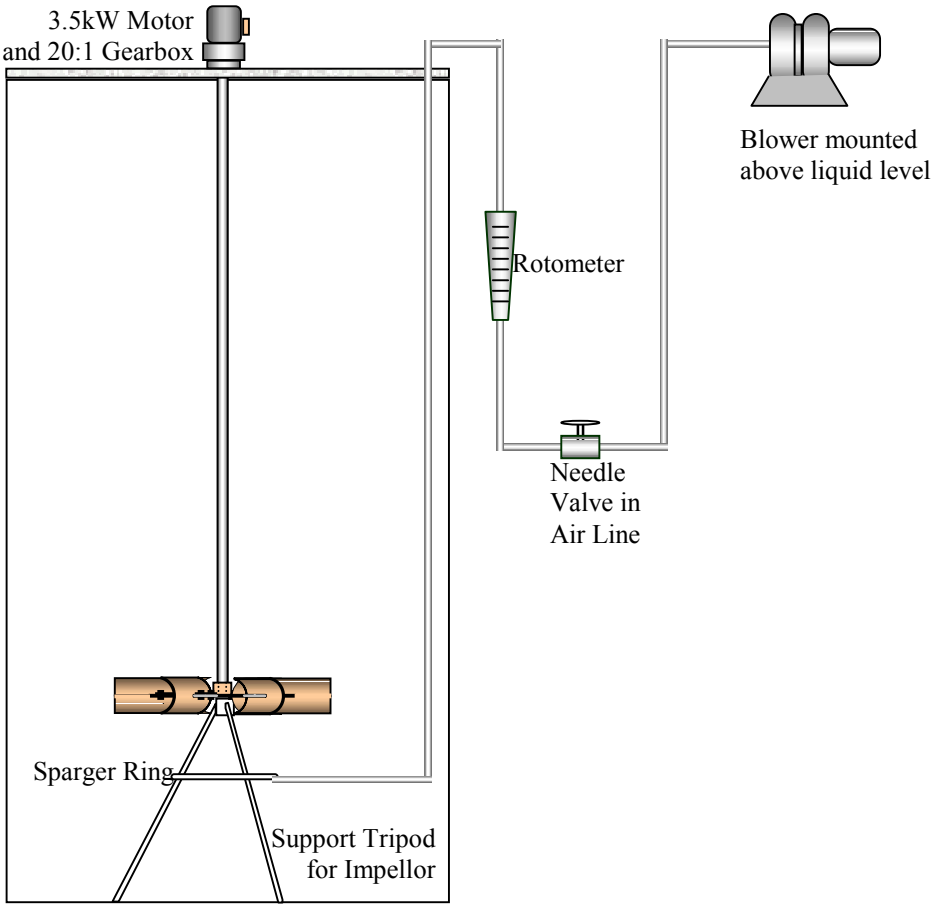


Figure 7.8 Air supply and distribution system for pilot plant

As depicted in Figure 7.9 - Figure 7.11 a thermosiphon heating system was also installed in the reactor tank. The purpose of this was to maintain the contents of the tank at a constant temperature without risking thermal shock of the biological culture that could occur if a high temperature electric element was used directly in the tank. The thermosiphon consisted of two vertical 3" diameter pipes installed on the outside of the tank, each containing a 7.5kW electric heating element inserted vertically inside the tubes (Figure 7.11). These two tubes then fed heated water to a coil inside the reactor tank, the turns of which were more concentrated in the region of high liquid flow generated by the impeller turbine. Due to the heating of the fluid inside the vertical legs of the thermosiphon and the subsequent cooling in the coils as the heat was transferred to the reactor vessel, a natural circulation of fluid flow was induced in the loop, thus transferring heat from the electric elements to the bulk reactor volume (Figure 7.9, Figure 7.10)

Figure 7.9 Impeller and thermosiphon coil installed in reactor tank

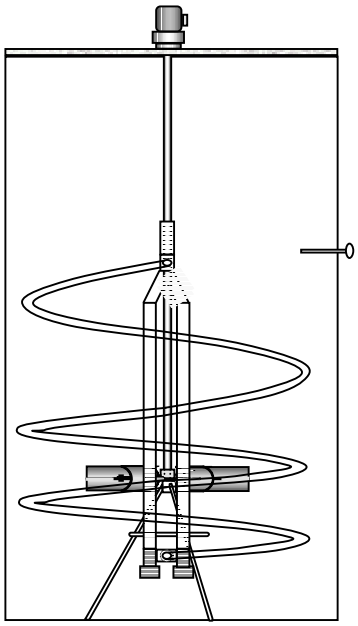


Figure 7.10 Thermosiphon installation in reactor tank

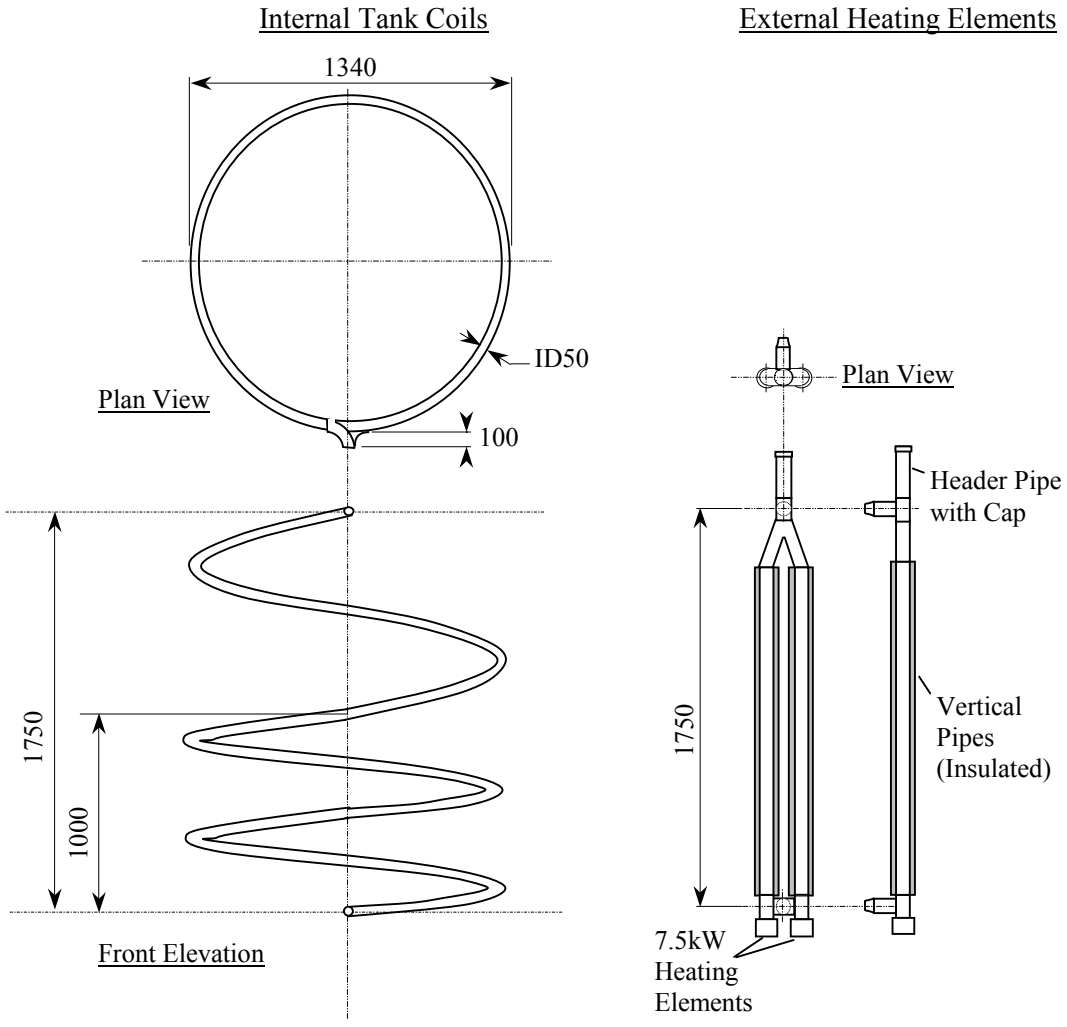


Figure 7.11 Thermosiphon design (all dimensions in mm)

7.3 EXPERIMENTAL PROCEDURE

7.3.1 OXYGEN MASS TRANSFER RATE DETERMINATION

After the appropriate modifications had been carried out on the process vessels, the pilot plant was installed at Fairlie Wool Scour as shown in Figure 7.1. Once all control and monitoring instrumentation has been installed, the overall layout of the pilot plant was as illustrated by the P&ID in Figure 7.13.

The oxygen transfer capacity of the aeration system used in the reactor vessel was determined using Sirolan CF effluent at pH 4.5, with no biological culture present.

The reactor was filled with $5m^3$ of feed effluent, and the mixture deoxygenated by gently mixing in 500g of sodium sulphate and 2g of cobalt chloride catalyst. In order to determine the oxygen transfer rate of the reactor over a range of operational conditions, the rate at which the dissolved oxygen concentration increased from zero to saturated was measured at different air flow and impeller speeds.

The aeration rates trialled utilised the following process conditions:

Table 7.1 Aeration rates tested

Trial	Air Flow [m^3/hr]	Impeller Speed [rpm]
1	25.5	38
2	32.3	38
3	30.6	60
4	32.3	60

The deoxygenation procedure detailed above was repeated between each trial.

Eckenfelder (Eckenfelder 1989) gives Equation (47) for the variation in dissolved oxygen concentration over time in an aerated vessel with no oxygen consumption:

$$C_S - C_t = (C_S - C_0)e^{-K_L a t} \qquad (47)$$

Where:

C_S = Saturated dissolved oxygen concentration in the liquid phase [mg/L]

C_t = Dissolved oxygen concentration at time = t [mg/L]

C_0 = Dissolved oxygen concentration at time = 0 [mg/L]

K_L = Liquid film diffusion coefficient [m/s]

a = Specific area of diffusion (Cross-sectional area of diffusion / Reactor volume) [m^2/m^3]

t = Time since aeration was started [s]

The relationship expressed in Equation (47) can then be linearised to Equation (48):

$$\ln(C_S - C_t) = \ln(C_S - C_0) - K_L a t \qquad (48)$$

which can be used to graphically determine the value of the gas-liquid mass transfer coefficient $K_L a$, as per Figure 7.12 (Milkie 1998).

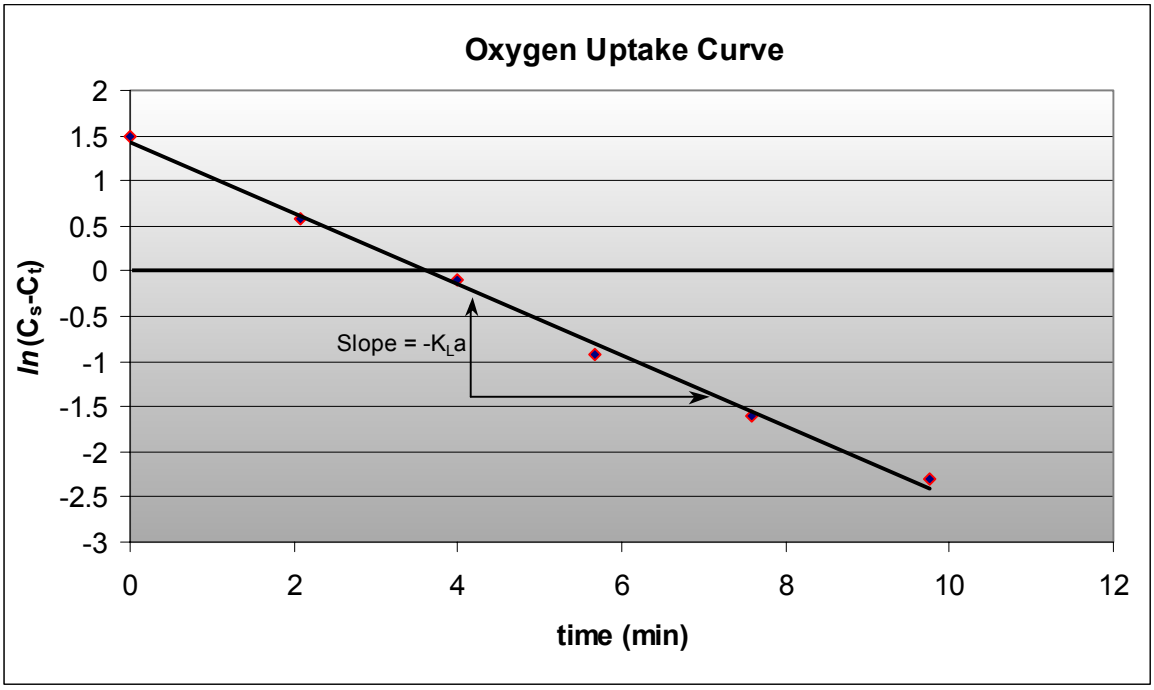


Figure 7.12 Graphical determination of gas-liquid mass transfer parameter $K_L a$.

7.3.2 BATCH BOD_5 DEGRADATION

In initial trials, batch degradation of BOD_5 in the pilot plant aerobic reactor was investigated. In order to achieve this, the reactor was filled with Sirolan CF liquor, seeded with approximately 5 litres of previously acclimatised culture, and the BOD_5 reduction and dissolved oxygen uptake were monitored over the initial 36 hours of aeration. Based on laboratory scale results this is not expected to be a commercially viable mode of operation. No pH neutralisation was carried out, and the feed was of undiluted Sirolan CF liquor.

7.3.3 CONTINUOUS OPERATION

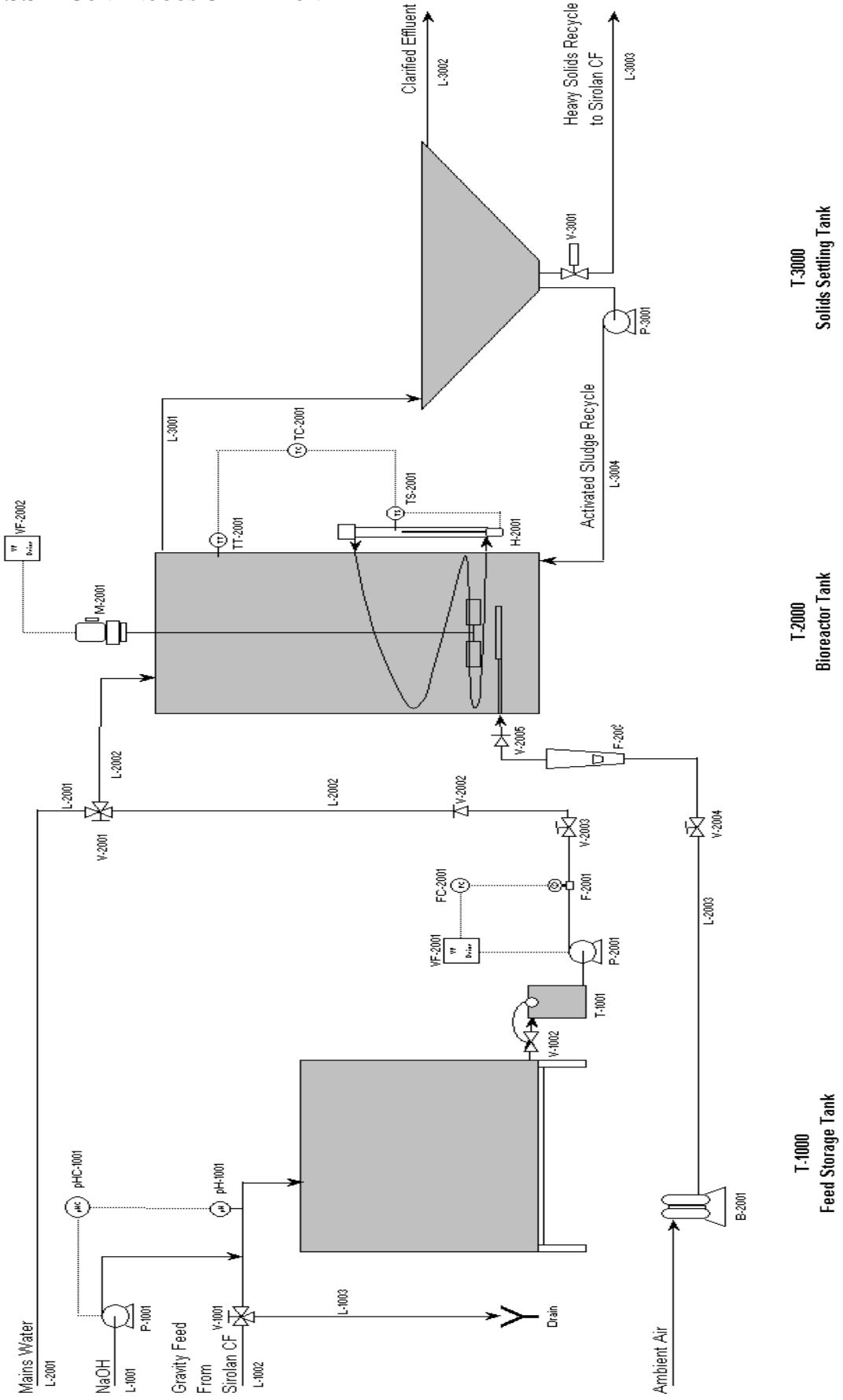


Figure 7.13 P&ID of 5,000L pilot plant

The P&ID in Figure 7.13 shows the gravity flow of effluent from the Sirolan CF decanter into the feed storage tank (T-1000). From T-1000, the feed flowed through a ball-cock (V-1002) into a constant level header tank (T-1001). The purpose of T-1001 was to provide the centrifugal feed pump (P-2001) with a constant suction head, thus allowing a more constant flow of effluent into the reactor vessel, independent of the level of effluent in the feed storage tank.

After a hydraulic residence time in the reactor tank (T-2000), determined by the flow rate of effluent through the feed pump P-2001, the treated effluent overflowed into the settling tank (T-3000). From the settling tank, clarified effluent flowed over the outlet weir to drain, while waste sludge was periodically discharged by use of a pneumatically operated knife-gate valve. Activated sludge was periodically recycled from the settling vessel to the reactor by use of a Sandpiper diaphragm pump (P-3001). This pneumatic pump was activated by a solenoid timer set to recycle a given quantity of sludge to the reactor vessel (T-2000) once every hour.

Due to the size of the feed storage tank used, the Sirolan CF pre-treatment process needed to be operated for five hours per residence time of the reactor to provide a constant supply of feed to the biological system. The hydraulic residence times used for these trials were 36, 48, and 75 hours, so the Sirolan CF process had to be run at its maximum throughput of $1m^3$/hr for five hours every two to three days to maintain consistent feeding. Operation of the Sirolan CF pre-treatment system proved labour intensive with constant attendance required during the five hours of operation to ensure consistent quality of the effluent product.

The process was fitted with a pH neutralisation system using automated addition of 50% active sodium hydroxide liquid (P-1001). This was used extensively to maintain pH in the reactor vessel at values > 6.5 at start-up and when operating at low hydraulic residence times.

The pilot plant was operated in this manner for a period of four months. Ten days of operation were allowed for the reactor to come to steady-state between any changes in hydraulic residence time and any measurement of BOD_5 reduction being made. Due to the high daily variation in the quality of effluent from the wool scour and Sirolan CF pre-treatment system however, the reactor was continuously in a state of flux, with any assumption of steady-state being a tentative one.

In order to achieve a range of feed concentrations to the reactor, dilution water was occasionally added to the feed effluent in the 5,000L feed storage tank. All results listed for

feed concentrations below 5,000mg/L BOD_5 were obtained by diluting the feed liquor to the concentration given.

7.3.4 SLUDGE SETTLING RATE DETERMINATION

In order to evaluate the gravity settling characteristics of the biological sludge produced in the aerobic reactor, settling velocity analysis was carried out.

This test used a large diameter one litre glass measuring cylinder, into which a sample of mixed liquor from the pilot plant reactor was added. After adding the sample to the cylinder, the settling velocity of a range of different sized biological flocs was determined by timing their descent through the centre section of the settler. In order to simulate the initial flocculation conditions present in a gravity clarifier, the mixed liquor was stirred manually with a glass rod at around 60rpm for 30 seconds prior to measuring the settling velocity.

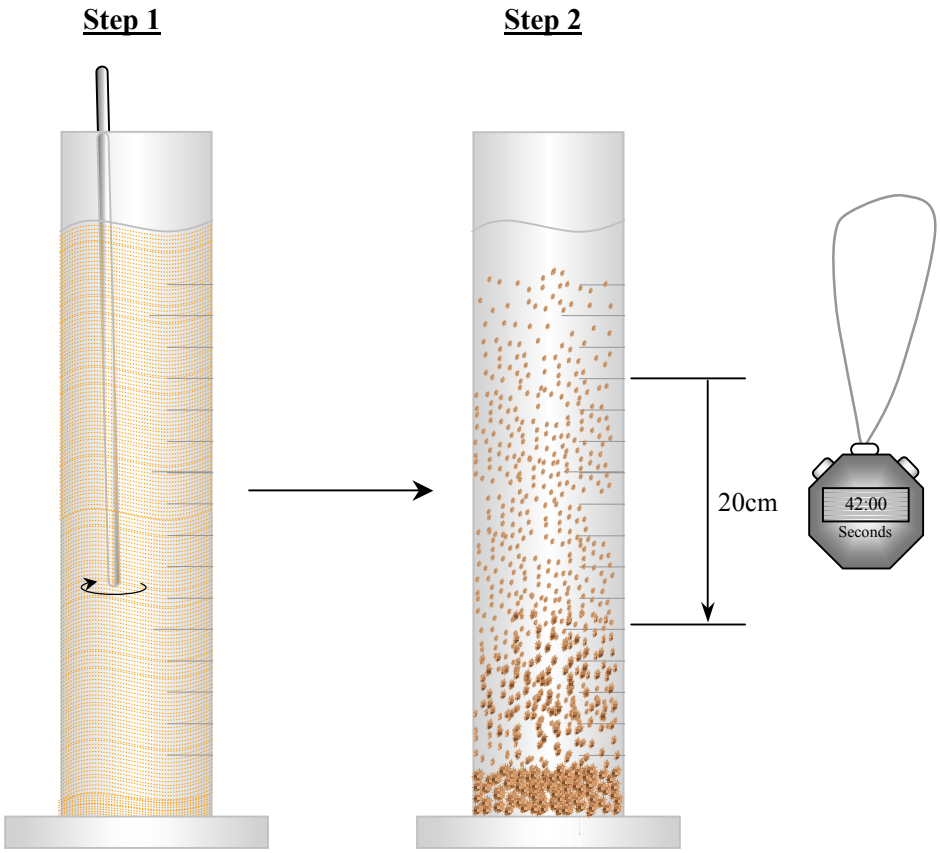


Figure 7.14 Settling velocity test procedure

7.4 RESULTS

While operating the 5,000L pilot plant, information was collected regarding BOD_5 removal, the effect of sludge recycle, the effect of intermittent feeding regimes, and process related factors such as foaming and biological neutralisation of the acidic feed.

The kinetic results of the 5,000L pilot plant re-enforced the general trend observed in the laboratory scale investigation. Most of the discoveries made at pilot plant scale were in terms of process related problems and operation of the plant, rather than bio-chemical kinetics and reaction rate data.

7.4.1 OXYGEN TRANSFER CAPACITY OF THE PILOT PLANT REACTOR

After installation of the pilot plant, analysis of the oxygen transfer capacity of the aerobic reactor was carried out as described in Section 7.3 to ensure sufficient oxygen was available to facilitate complete aerobic BOD_5 removal.

The tests carried out showed the following oxygen transfer capabilities for the given aeration rates at 15°C:

Table 7.2 Oxygen transfer capacity of the pilot plant reactor

Air Flow to Reactor [m^3/hr]	Gas Dispersion Impeller Speed [rpm]	Mass Transfer Coefficient K_La [m/s]	Oxygen Transfer at DO = 1ppm [g_{O_2}/hr]
25.5	38	0.22	795
32.3	38	0.28	1,005
30.6	60	0.39	1,415
32.3	60	0.65	2,323

7.4.2 INITIAL BATCH TRIALS AND pH CONTROL

Investigations carried out with batch aeration of acidic (pH 4.5) Sirolan CF effluent did show up to 16% reduction in BOD_5 over two days of aeration. A drop in dissolved oxygen concentration after five hours indicated the growth of an aerobic biological culture even at this low pH (Figure 7.15). After five days of batch operation as per Figure 7.15, the pH had risen from pH 4.5 to pH 5.2, indicating that either biological buffering or volatilisation of acids was occurring.

In none of the trials carried out under batch or continuous flow conditions, with hydraulic residence times of less than 100 hours, was it possible to achieve greater than 20% BOD_5 reduction at a pH below 6.0

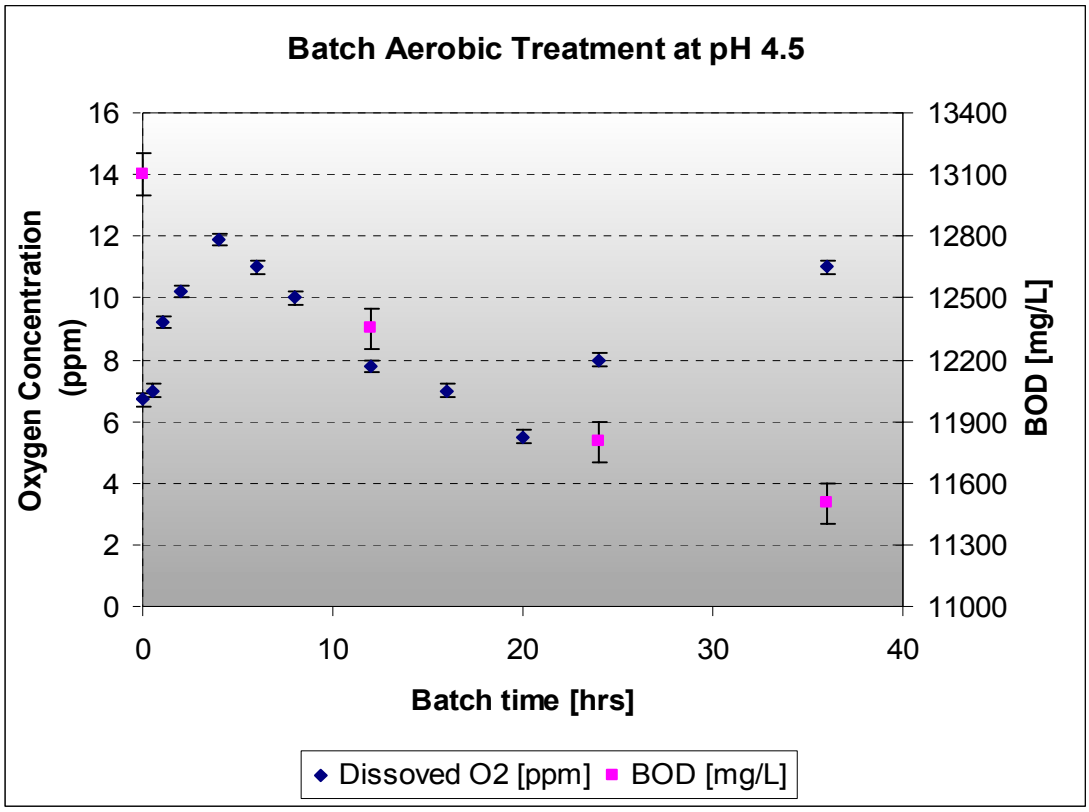


Figure 7.15 BOD_5 reduction at low pH

7.4.3 PILOT PLANT PERFORMANCE UNDER CONTINUOUS OPERATION

When operating continuously with pH neutralisation, the 5,000L reactor gave a consistent result of 50 – 60% BOD_5 removal with a 36 hour residence time, and 85 – 95% BOD_5 removal at 50 hour residence time. At 50 hour residence time only occasional addition of sodium hydroxide was required to maintain pH > 6.5.

Table 7.3 Typical results of the pilot plant reactor under continuous operation

Residence Time [hrs]	pH	BOD_5 In [mg/L]	BOD_5 Out [mg/L]	BOD_5 Removal
36	5.6	10,500	8,200	22 %
36	6.5 – 8	10,000	4,000	60 %
36	7 – 8	8,900	3,850	57 %

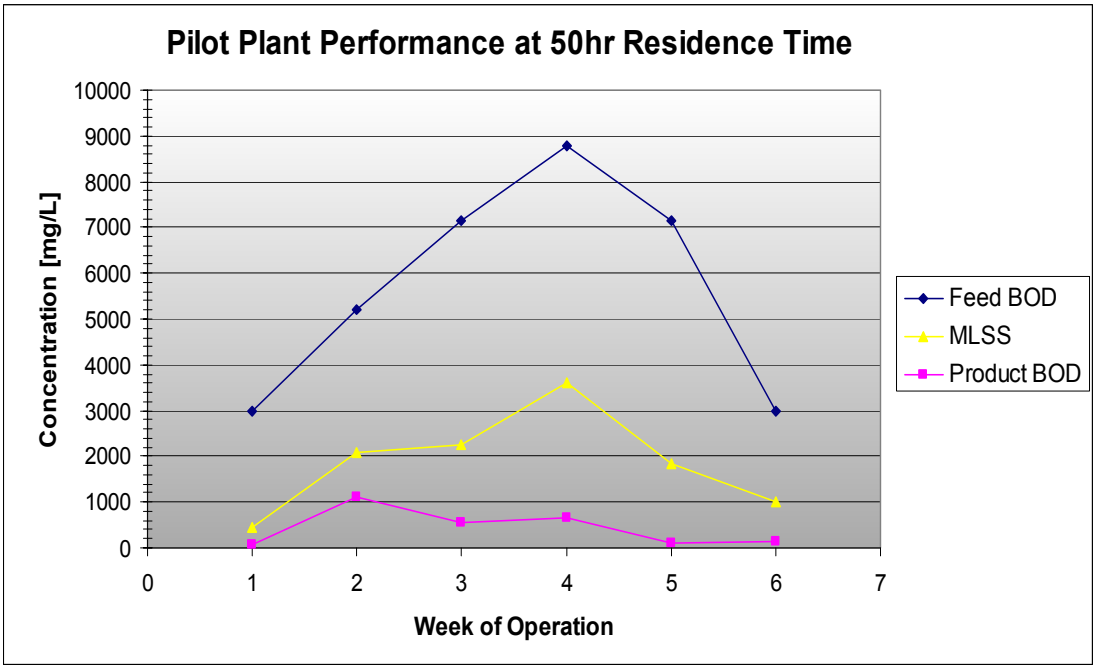


Figure 7.16 Results of the 5,000L pilot plant

By using the oxygen transfer characteristics of the aeration system as determined in Section 7.4.1 above, the oxygen consumption of the reactor could be determined under any given operating condition by measuring the dissolved oxygen concentration and setting the air flow and agitator speed to one of the sets of conditions given in Table 7.2. The corresponding value of K_La could then be used to determine steady-state oxygen transfer to the liquid phase. Comparison of these results showed much closer stoichiometric agreement between COD uptake and oxygen uptake than between BOD_5 uptake and oxygen uptake.

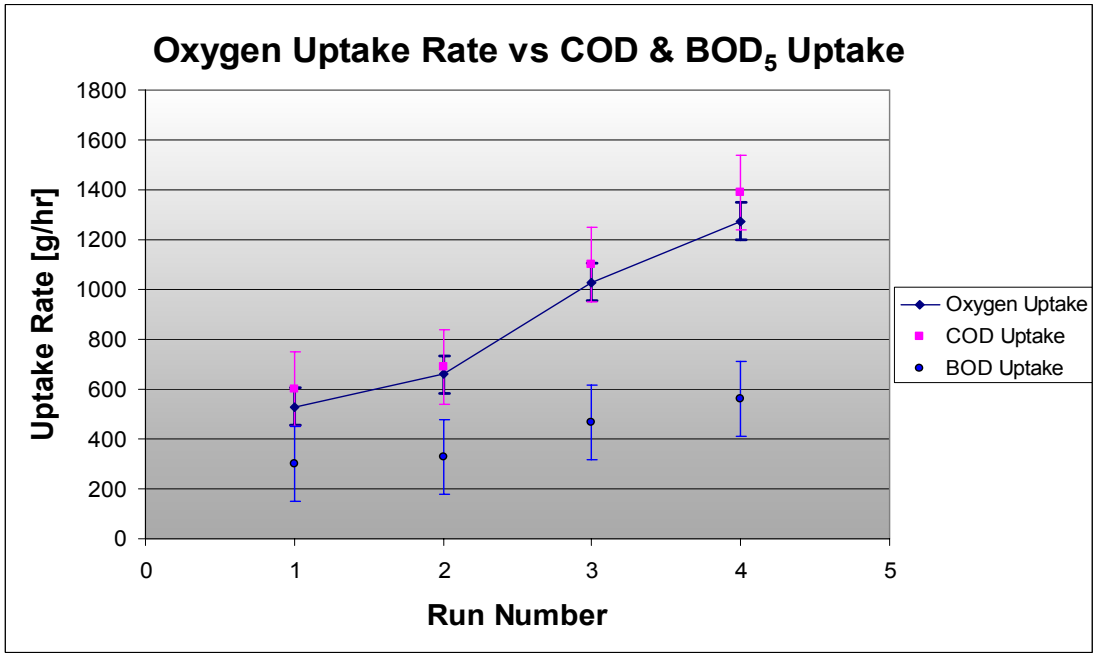


Figure 7.17 Oxygen uptake vs BOD_5 and COD uptake

7.4.4 FOAMING

One problem encountered early on in pilot plant operation was the level of foam generated by aeration of the mixed liquor. Under normal operating conditions, the foam level reached a stable equilibrium 400 – 600mm above the height of the liquid surface (Figure 7.18)

Figure 7.18 Normal foam level in pilot plant reactor

Periodically however, the foam level would break equilibrium and rise to the point where it overflowed on a continuous basis from the vessel and accumulated on the ground. Mechanical foam breakers consisting of flat plastic or metal bars mounted horizontally on the rotating impeller shaft (centre of Figure 7.18), approximately 300mm above the liquid surface, proved effective at suppressing the foam in all but the most extreme cases of foam generation. An ***increase*** in the air supply rate to the reactor also proved effective in minimising foam generation. This was attributed to the larger bubble size produced by increasing the sparge rate. Maintaining constant gas feed rate and slowing the gas distribution impeller achieved the same effect. The larger bubbles resulted in a less stable foam matrix, while increasing the surface turbulence and the airflow through the foam layer. Figure 7.18 shows this effect, with high air feed rate creating a turbulent zone on the surface of the liquor (immediately above the aerator) over which the foam layer is not self-sustaining.

The highest levels of foam generation were observed to occur when the feed rate was significantly reduced from normal (e.g. at hydraulic residence times of over 100 hours), or

when the reactor was not fed for a number of days. In these cases re-commencement of normal feed rate to the reactor reduced foam generation to an acceptable equilibrium height of foam above the liquor within 1 – 2 minutes.

7.4.5 TEMPERATURE CONTROL

As with the laboratory scale reactor, the 5,000L pilot plant was fitted both with temperature monitoring and temperature control. As the pilot plant reactor was situated outdoors and was to be operated through the months of March – August (New Zealand's winter) this was considered a necessary precaution. Although the use of a PID temperature control loop did enable kinetic results to be recorded within a consistent temperature range, supplemental heating was not often required as the temperature of the reactor typically maintained itself above the 20°C set point of the temperature controller.

7.4.6 SLUDGE CHARACTERISTICS

The floc structure of the bacteria growing in the pilot plant reactor showed gravity settling characteristics comparable to rapid settling, non-bulking municipal activated sludge [Water_Environment_Federation, 1998 #10] with settling velocities measured in the range of 16cm – 30cm per minute.

Figure 7.19 Sirolan CF-B pilot plant settler.

Figure 7.20 Floc formation in pilot plant settler

Figure 7.19 shows the pilot plant settling-tank from the feed end. The mixed liquor overflowing from the reactor vessel was fed to the settler via the large stainless steel pipe in the foreground. The mixed liquor entered the settling vessel via a flow-distribution weir (see Figure 7.6 for detail), and the clarified supernatant then overflowed from a v-notch weir in the opposite end of the vessel (Figure 7.6 and Figure 7.19). In the case depicted in Figure 7.19 and Figure 7.20, sludge removal from the settler had been temporarily suspended, thus deliberately overloading the settler with biological sludge in order to illustrate the nature of the biological flocs formed. It can be seen in these figures that the well-defined sludge blanket filled the hopper to the liquid surface at the feed end of the settler. At a feed rate of 100L/hr the biological flocs settled sufficiently to be collected (i.e. not overflow with the supernatant) after only 50cm of travel from the inlet pipe. On scaling up to commercial scale, this correlates to a minimum surface area for settling in a 10,000L/hr unit of ~ 30m^2.

7.5 DISCUSSION

7.5.1 BATCH OPERATION OF THE PILOT PLANT REACTOR

Although initial tests were carried out into the degradation of BOD_5 by operation of the pilot plant reactor in batch mode, this was only ever intended for the purpose of collecting operational data under these conditions. The results of these tests upheld the initial hypothesis that this would not be a feasible mode of operation in a full-scale installation.

As substantiated by the substrate inhibition results presented in Section 6.3, the use of the reactor in batch mode, where the microbial culture encountered high strength effluent at the beginning of each batch, did not prove conducive to optimum BOD_5 removal.

Moreover, at the time of batch testing, no supplemental pH neutralisation was available, so each batch started at the low pH of the Sirolan CF pre-treated feed liquor.

These conditions combined to produce the low level of BOD_5 degradation observed in all batch trials. Some self-neutralisation of pH was observed in the reactor under batch conditions, but not at hydraulic residence times practical for commercial application. Whether this neutralisation was caused by biological activity or merely by air stripping of volatile acids was not determined. In all cases where the batch of effluent was left aerated in excess of five days after initial seeding and start-up, the pH rose from the pH 4.0 – 4.5 start point to around pH 5.5 after five days of aeration. Testing under continuous flow conditions both at laboratory scale (Section 6.3.3) and at pilot plant scale (Section 7.4.3) suggested that even this increased pH after five days of aeration was insufficient to allow optimal growth of the mixed biological culture required for BOD_5 removal.

7.5.2 PILOT PLANT PERFORMANCE UNDER CONTINUOUS OPERATION

As can be seen from the batch operation results in Section 7.4.2, the pilot plant did not initially include online pH monitoring or control. Although this was found to be seldom required at laboratory scale due to the self-buffering action of the reactor, the greater variability of the feed strength to the pilot plant scale reactor resulted in frequent problems with decline of the biological culture due to the inability of the microbial culture to buffer the acidity of the feed under sudden increases in effluent strength. As can be seen by comparison of Table 7.3 with Figure 7.16, this problem was much more significant at lower hydraulic

residence times. At 36 hour residence time the BOD_5 removal was observed to drop off to almost 20% at times of low pH in the reactor.

The results illustrated in Figure 7.16 represent six weeks of stable operation with pH control by automated sodium hydroxide addition. Although only small quantities of sodium hydroxide were used (< 10L per week), at a 50 hour residence time this proved sufficient to supplement the natural buffering activity of the biomass in the reactor under conditions of fluctuating feed strength.

During the six weeks of continuous operation at a 50 hour residence time, the product BOD_5 fluctuated between 110 and 1,100 mg/L. With the exception of a slight increase in effluent BOD_5 in some instances where the feed BOD_5 was increased dramatically over a short period of time, the effluent BOD_5 was observed to be largely independent of feed strength. As has also been reported in literature (Eckenfelder 1989), this was observed to be due to the higher feed concentration resulting in a higher equilibrium biomass concentration in the reactor basins giving a consistent overall residual BOD_5 in the effluent (Figure 7.16).

Overall, the pilot plant performance observed at 50 hour residence time was encouraging, with pre-treated influent of the strength expected in industry (BOD_5 < 8,000mg/L) consistently being reduced to BOD_5 levels in the effluent of less than ~700mg/L. The overall BOD_5 removal under these conditions ranged from 92 – 98 %.

Influent of strength higher than 8,000mg/L BOD_5 was observed to cause deterioration in the effluent BOD_5 of the biological system. This is consistent with results obtained at laboratory scale, which suggest that excessive feed strength has a toxic effect on the biological culture in the reactor (Figure 6.21, Figure 6.27).

Examination of the oxygen transfer capabilities of the reactor in Section 7.4.1 resulted in the conclusion that the maximum oxygen transfer capacity observed in the pilot plant was in the order of 2,300g/hr. Assuming that COD uptake is stoichiometric with oxygen uptake of the culture (supported by the results presented in Figure 7.17), this level of oxygen transfer is only able to support up to an equivalent 2,300g/hr of COD removal in the reactor.

At the 36 hour residence time initially utilised, this indicates a maximum possible COD uptake of 16,500mg/L, which corresponds to a BOD_5 reduction of approximately 6,500mg/L (See Appendix II for correlation of BOD_5 to COD). When operating at a 50 hour hydraulic residence time however, the amount of oxygen transfer available corresponds to a maximum

COD uptake of 23,000mg/L, which in turn corresponds to a maximum possible BOD_5 removal in the reactor of around 9,000mg/L. This result for the 50 hour residence time corresponds closely to the results presented in Figure 7.16, in which BOD_5 reduction drops off at these high feed substrate concentrations.

Due to this observation of potential oxygen transfer limitation, it cannot be firmly concluded that the reduction in performance of the pilot plant reactor at high feed substrate concentrations was due to substrate inhibition alone. In some cases the oxygen transfer capability of the reactor may have been the limiting factor. The strain on the oxygen transfer capacity of the reactor was also increased by the excessive generation of foam in the reactor periodically requiring that the aeration rate be reduced to prevent foam overflow from the reactor vessel. In instances where high levels of foam generation were encountered, the gas dispersion impeller was slowed to 38rpm, while the airflow was maintained at 32.3m^3/hr. From Table 7.2 it can be seen that the resultant oxygen transfer under these conditions would have been effectively half that available with the gas dispersion impeller operating at full speed. This raises the probability that under excessive foaming conditions the reactor had insufficient oxygen transfer capacity to facilitate complete BOD_5 removal.

7.5.3 EXCESS FOAM GENERATION

As has already been observed, significant problems were encountered with excessive levels of foam generation from the aerobic reactor vessel. The two main concerns raised by this were discharge of effluent to the environment via foam spills, and reduction in reactor capacity due to the reduced aeration rates required during times of high foam generation.

Discharge of foam to the environment was of significant concern due to the extent to which the liquid contents of the reactor were removed in the foam matrix. In one instance where the aeration system was left operating at full capacity unattended, after two days of continuous foaming the reactor had lost over one third of its liquid contents onto the ground (and subsequently into the local stormwater drain) in the form of foam.

Observations made over the three months of continuous operation indicated that foam generation was generally highest at times of low or no feed to the reactor. In these cases where, for instance, the reactor had not been fed over a weekend, resulting in excessive foam generation, re-commencing normal feed rate of Sirolan CF liquor reduced the foam generation to manageable levels, or stopped it altogether, within 1 – 2 minutes.

Attempts to utilise rotating mechanical foam breakers in the headspace of the reactor vessel did result in reduced overflow of foam but, in most cases, once these had become swamped in foam their effectiveness was decreased significantly and the foam continued to overflow, albeit at a lower rate.

The most successful such approach was to have multiple, staged rotating mechanical breakers mounted at different heights above the liquid, but even this was not effective in all instances.

Excessive foaming was a problem that was not fully resolved at the 5,000L pilot plant scale. Towards the end of the pilot plant operation a second product overflow port was installed halfway down the reactor tank, so that the reactor could be operated at 2,500L capacity with approximately 1.5m of freeboard above the liquid surface. This provision of extra height in which the foam could be contained while it drained and destabilised under its own weight, combined with rotating mechanical foam breakers 1.2m above the liquid surface, proved sufficient to contain the foam generated under any conditions experienced at this scale. By allowing a large amount of static head in the reactor for foam build-up, the foam was given sufficient time to drain and destabilise under its own weight before contacting the mechanical foam breaker in the top of the reactor. The result of this was that, in most instances, the equilibrium foam height remained below the mechanical foam breaker and when it did rise into the path of the rotating paddle, the foam had had sufficient time to drain and weaken that the foam breaker worked much more effectively than when placed closer to the liquid surface.

Figure 7.21 Increased freeboard for foam containment

7.5.4 TEMPERATURE CONTROL

As reported in Section 7.4.5, the temperature of the reactor was typically maintained itself above the 20°C set point of the temperature controller. As a result of this, it was deemed unnecessary to include temperature control on future designs. Supplementary heating would be particularly unwarranted in situations where the wool scour effluent flowed through a 'flow-down heat exchanger' for recovery of heat from this stream prior to discharge to the effluent treatment plant (as is the case with most modern wool scours). In these cases, if supplemental heating was required, this could be provided by limiting the amount of heat recovered from the feed prior to being passed to the bioreactor.

7.5.5 SLUDGE CHARACTERISTICS

It is a requirement of almost all activated sludge systems that they produce a bacterial floc that can be removed from the mixed liquor by gravity settling. This is generally achieved by maintaining a microbial population that is able to flocculate into large clumps or 'flocs' of biomass. These flocs then settle many orders of magnitude faster than the bacteria would otherwise do if growing independently. Dispersed growth is a problem encountered by some activated sludge processes where the bacteria do grow independently rather than form into flocs. This results in unacceptably high suspended solids concentrations in the treated effluent, and the subsequent inability to maintain biomass concentration in the reactor can lead to catastrophic reactor washout and treatment plant failure.

In all cases where the pilot plant reactor was operating in continuous flow mode with pH > 6.0, the microbial population formed large 1 ~ 5mm diameter flocs, which settled out very effectively in the gravity clarifier vessel used.

The settling rate of the flocculated biomass was measured at 16 – 30cm / min for the range of floc sizes encountered in the pilot plant reactor. It must be noted that, due to the dark colour of the effluent, only the settling rate of solids within 4 – 6mm of the wall of the glass test cylinder could be measured. This introduces the risk of wall effects significantly reducing the settling velocity observed under test conditions. The application of these test results to clarifier design could subsequently result in a conservative design. Potentially of more concern is the observation that, due to the relatively large flocs formed and the velocity at which they settled in the glass test cylinder, clarified liquor was forced up between the flocs at high velocity. These high velocity counter current flows resulted in the formation of significant recirculation currents within the test vessel. These currents were observed to be

moving at vertical velocities between of 20 – 80cm/min, and therefore had the potential to interfere greatly with the results obtained in the settling rate determination tests. While every effort was made to measure only settling velocity of biomass flocs which were unaffected by these recirculation currents, the potential presence of uniform annular currents, in particular flowing up through the centre of the cylinder and down the walls, may have gone undetected and thus affected the results achieved.

From the observations of sludge separation at the pilot plant scale, it was concluded that the effluent being treated was not overly susceptible to outbreaks of the two most common forms of sludge quality deterioration; filamentous bulking (Seka *et al.* 2001) or dispersed microbial growth (Clauss *et al.* 1998). At no stage during the pilot plant trial did these conditions occur. For a firm conclusion regarding this matter, observation of a continuously operating plant over the space of at least one year of operation would need to be carried out.

7.5.6 KEY DESIGN PARAMETERS FOR SCALE-UP

From the work carried out at this scale it was determined that a $1m^3$/hr demonstration plant could be constructed with 50,000L of aerobic hydraulic residence time. In such a plant the surface area available for foam generation should be minimised, and at least 1m of gravity head should be provided above the liquid surface for foam draining and destabilising. Temperature control is not considered necessary on future models, but automated pH control was identified as a necessity under fluctuating feed conditions.

8 50,000L DEMONSTRATION PLANT STUDIES

8.1 INTRODUCTION

The final experimental phase involved constructing a fully operational 1,000L/hr capacity demonstration plant. Based on the results obtained at laboratory and pilot plant scale, this plant had a total aerated reactor volume of 50,000L, made up of the two 25,000L PVC water tanks shown in Figure 8.1. The two separate reactor vessels were configured so that they could be operated in series or parallel, whichever gave the most effective and robust operation. The aim of this investigation was to implement and evaluate solutions to process problems observed at the 5,000L pilot plant scale, and to investigate the continuous BOD_5 removal of a commercial scale unit under realistic operating conditions.

8.1.1 OVERVIEW OF DESIGN

Based on the results of the 5L and 5,000L scale experimental phases, a third experimental plant was designed and installed at Fairlie Wool Scour, Timaru Ltd. This plant consisted of two 25,000L PVC water tanks fitted out with venturi injectors for aeration and liquid mixing.

Figure 8.1 Aerobic reactor tanks of 50,000L Sirolan CF-B plant

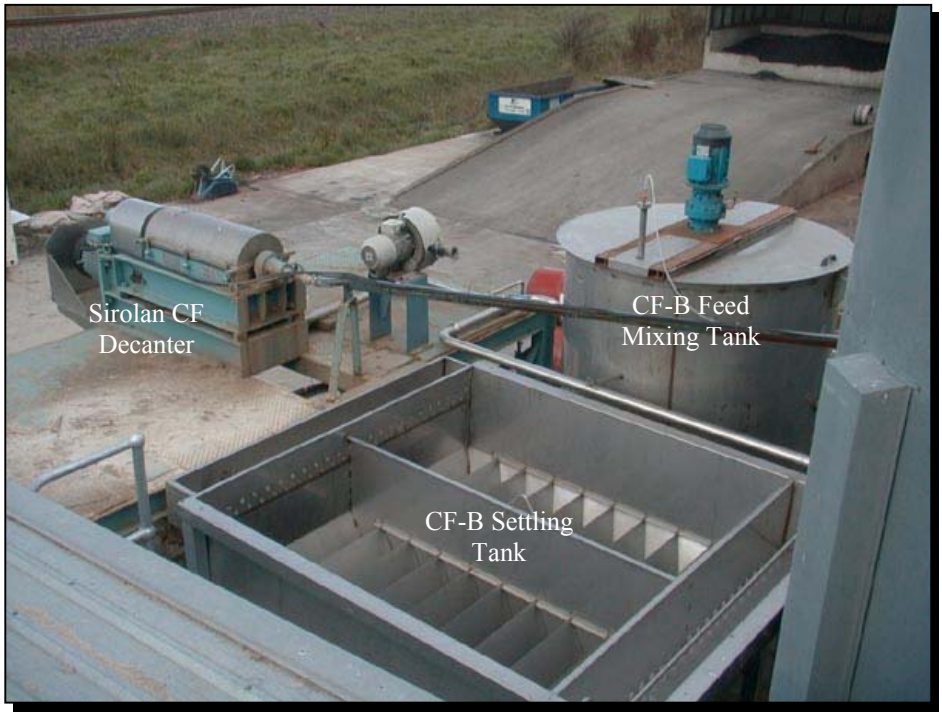


Figure 8.2 Sirolan CF-B 50,000L plant ancillary vessels

The purpose of the 50,000L plant was twofold. The primary goal of this investigation was to implement process improvements identified as lacking in the 5,000L model. Secondary, was the need to have a treatment plant of sufficient size to treat the entire heavy flow-down of a small wool scour operating reliably in industry. This would illustrate the particular difficulties associated with continuous operation, and provide a reference site for commercial exposure of the process to potential clients.

8.2 DESIGN OF THE 50,000L PLANT

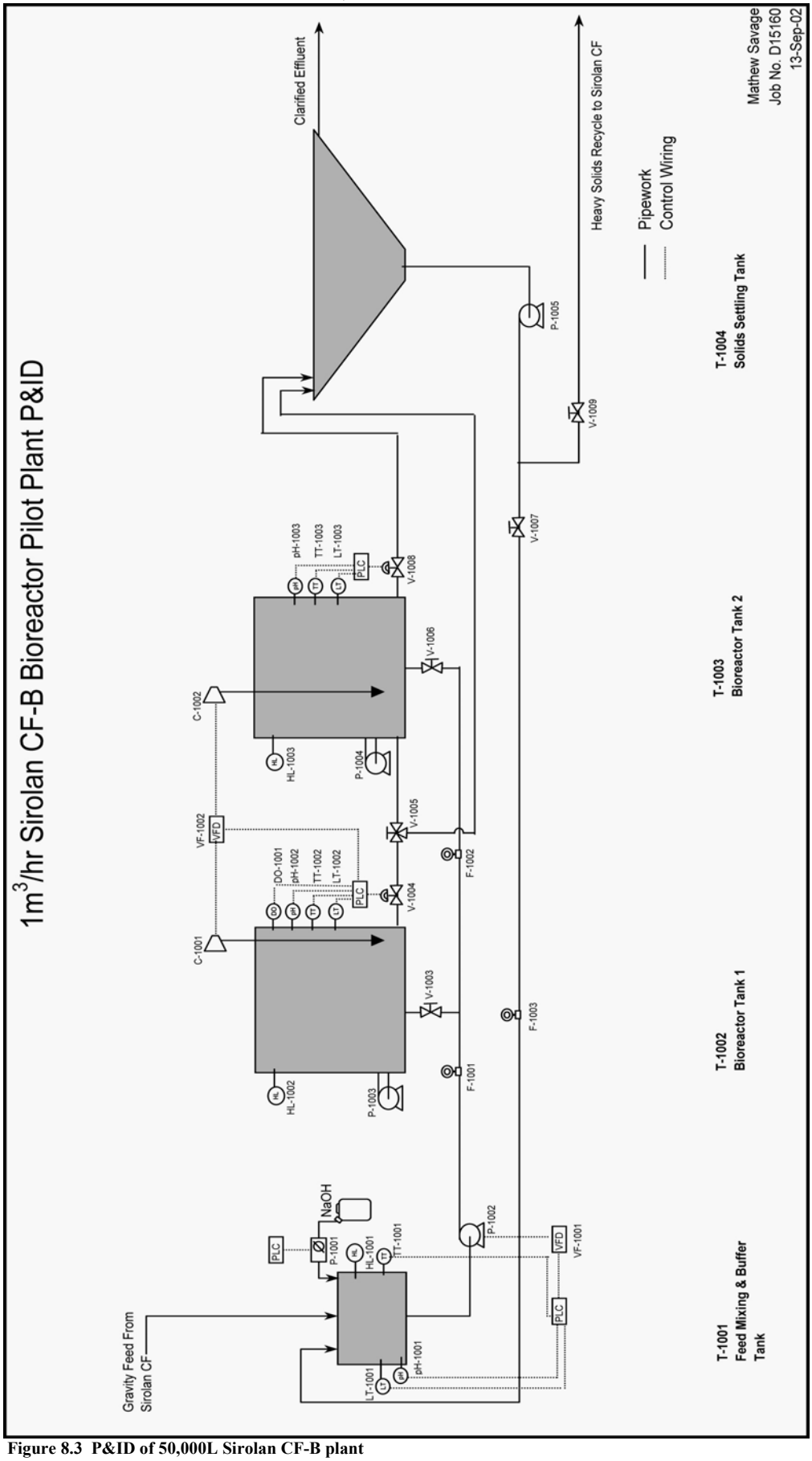


Figure 8.3 P&ID of 50,000L Sirolan CF-B plant

8.2.1 TWIN TANK DESIGN

As pictured in Figure 8.1, the reactor vessels of the 50,000L plant consisted of two 25,000L PVC farm water tanks. The implementation of a 2-tank design was primarily in order to investigate the option of running the process as separate tanks operating either in series or in parallel. Due to the low capital cost of the plastic tanks, this configuration also presented the lowest capital cost for a plant capable of treating up to $1m^3$/hr of effluent.

The use of two separate digestion tanks raised the possibility of using these tanks either in series or in parallel configuration, as shown by Figure 8.4 and Figure 8.5 respectively. The process was designed and built with piping and valves in place to allow either series or parallel operation to be maintained at any time (Figure 8.3, Table 8.1).

The following valve configurations were used to give either series or parallel operation of the two reactor vessels. For location and function of each valve listed see Figure 8.3.

Table 8.1 Valve configurations for Series / Parallel operation

Valve	Series Operation	Parallel Operation
V-1003	Open	Open
V-1004	Open	Open
V-1005	T-2000 → T-3000	T-2000 & T-3000→ T-4000
V-1006	Closed	Open
V-1008	Open	Closed

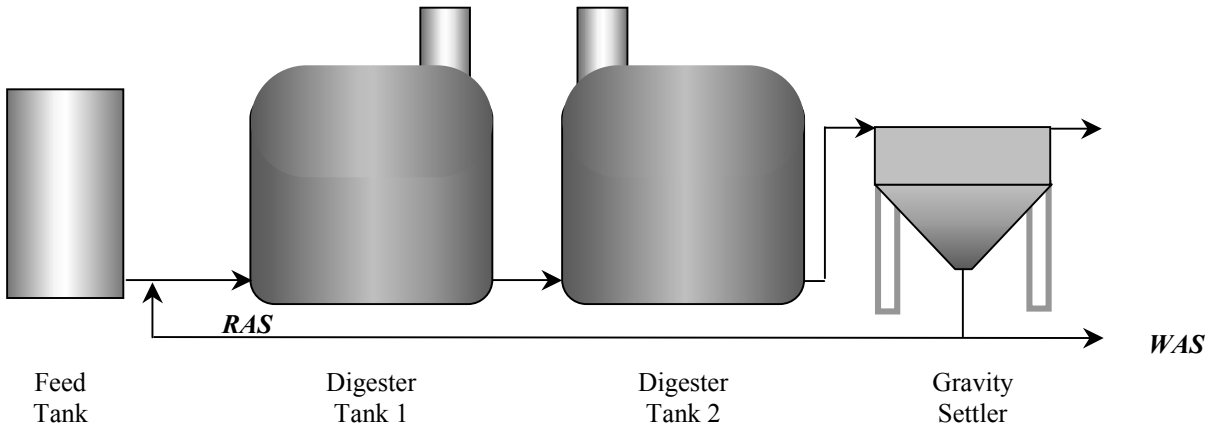


Figure 8.4 25,000L digester tanks in series

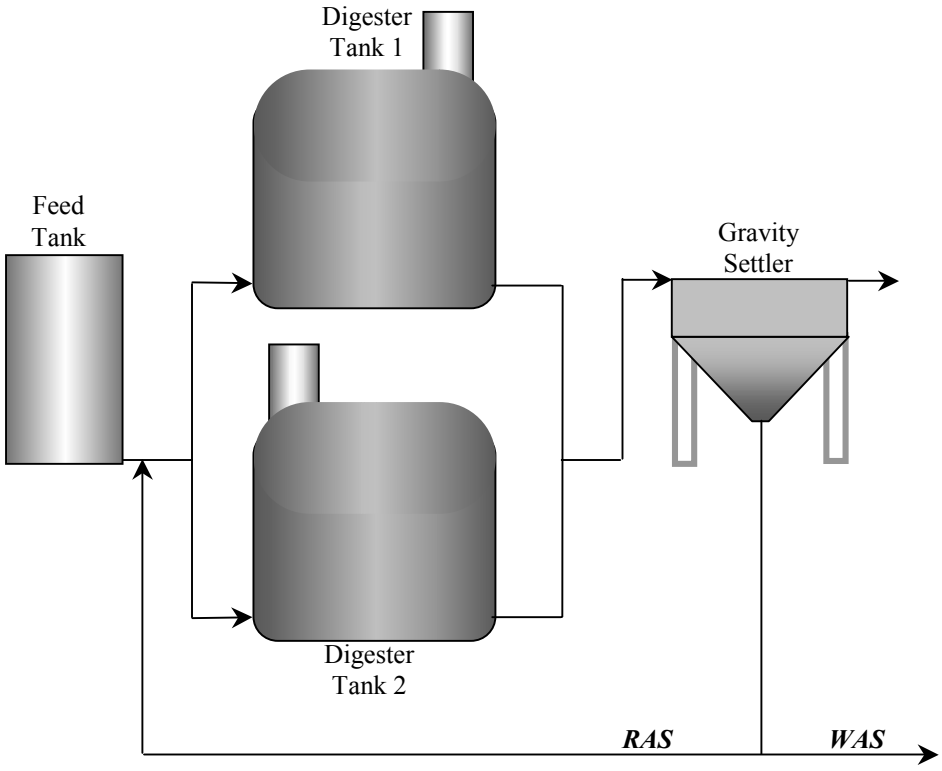


Figure 8.5 25,000L digester tanks in parallel

8.2.2 AERATION SYSTEM

Due to the type of tanks used in this plant, and the potential use of rectangular in-ground pits in the full-scale process design, mechanical mixing by a turbine agitator was considered not to be feasible as a means of gas dispersion. As a replacement, Körting 4-path venturi jet injectors were selected as the means of gas – liquid mixing. These systems consist of three parts:

1. A venturi manifold with no moving parts which is installed inside the tank.

The aeration system used a set of venturis built into a common manifold to entrain fine air bubbles in a jet of water, which is in turn injected into the main body of the tank. This is performed in such a manner as to facilitate both oxygen transfer and bulk liquid mixing. Each individual venturi operates as illustrated in Figure 8.6.

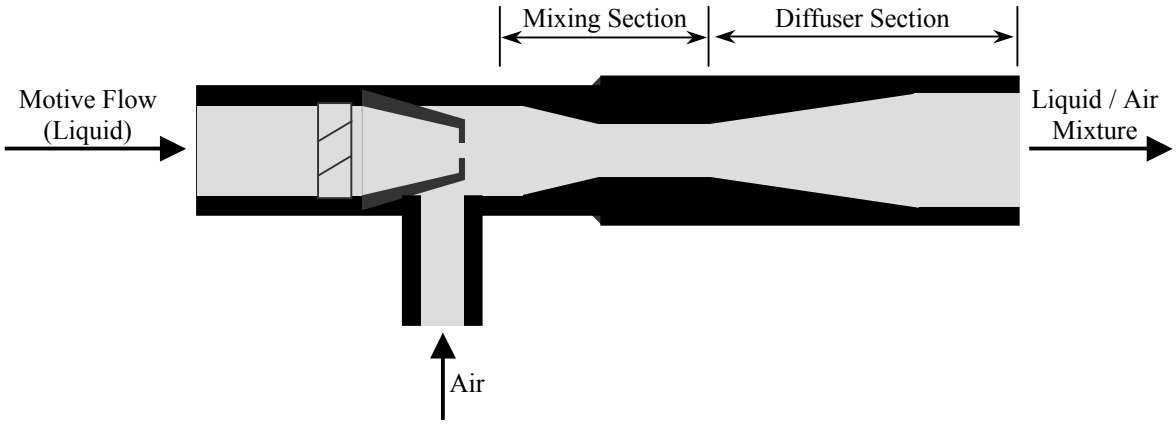


Figure 8.6 Internal construction of venturi injectors

These venturi units were combined into a common manifold, containing 4, 6, or 9 separate venturi injectors with common air and motive flow supplies. The pumped motive flow liquor typically enters through a main pipe in the bottom of the manifold while the air supply is drawn into the top of the manifold as pictured in Figure 8.7.

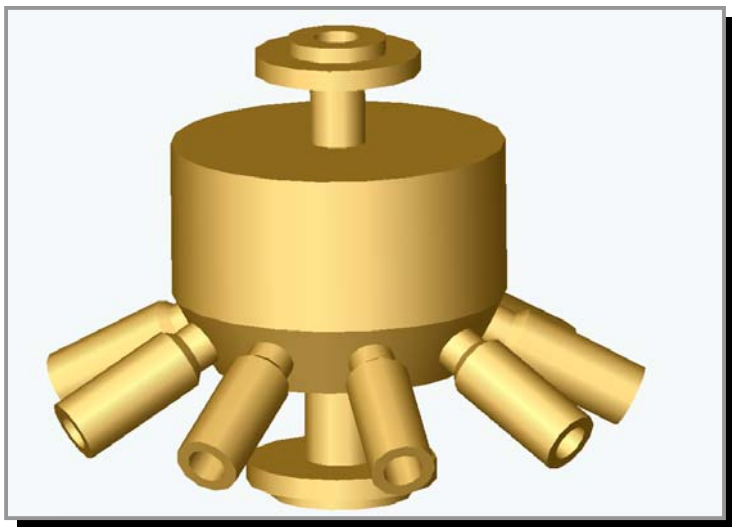


Figure 8.7 Körting 9-path venturi injector manifold

2. A recirculation pump mounted outside the tank.

The motive flow supplied to the injector units was provided by a centrifugal pump located outside the aeration tank. The capacity of this pump was specified by the suppliers of the venturi injectors based on the overall oxygen transfer requirement. In this case, a 40m^3/hr capacity Southern Cross centrifugal pump was used on each of the 25,000L aeration tanks (Figure 8.8).

Figure 8.8 Recirculation pumps used on 50,000L demonstration plant

3. An air supply mounted outside the tank, above the water level.

For maximum operating efficiency, the air feed to the aeration modules required compressing to the static pressure at the point of injection. As the injectors were submerged under three metres of liquid, a 29kPa pressure increase was required over the air supply. This pressure requirement along with the air requirement of 300Nm^3/hr, raised the option of using an inexpensive compressor designed for the automotive industry, namely a 2-litre Toyota Corolla supercharger per aeration tank. Two of these were obtained secondhand for the purpose.

Figure 8.9 Compressor locations between aeration tanks

Aeration System Configuration

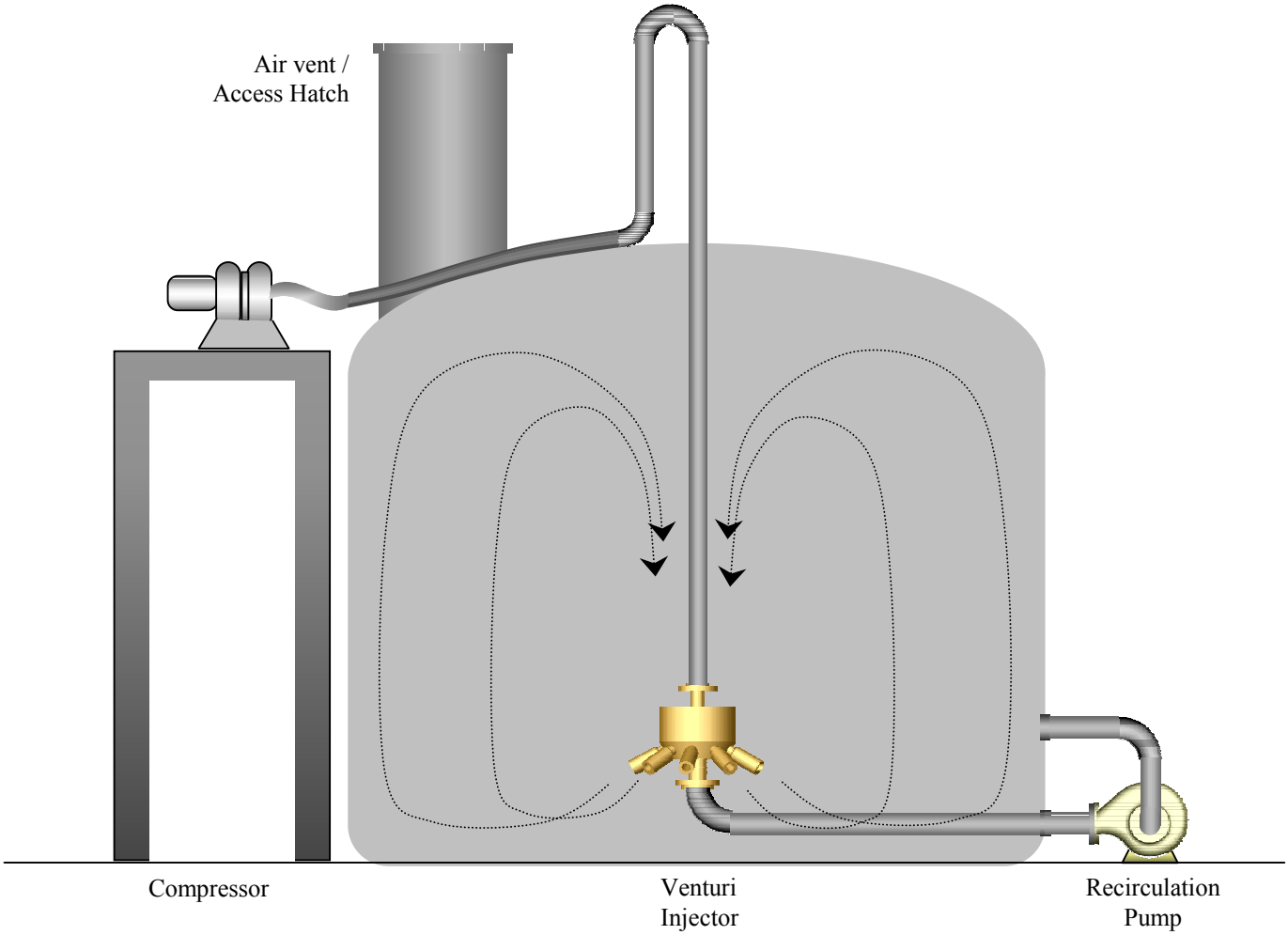


Figure 8.10 Aeration and mixing systems

The layout of the aeration system as applied to each of the 25,000 litre tanks is shown in Figure 8.10. The liquid / air jets from the downward pointing diffusers of the venturi manifold provide both mixing and aeration of the tank contents. Both tanks were set up in an identical manner. As it was possible for the tanks to operate at liquor levels as high as half way up the air vent stack (Figure 8.10 and shown in stainless steel in Figure 8.9), the air feed line utilised a 1.5m high inverted U-bend to prevent backflow of liquor into the compressors.

8.2.3 SETTLING SYSTEM

The gravity settling system used is illustrated in Figure 8.2. This was based on an existing ANDAR hopper-bottomed settling tank design and included inclined lamella plates for improved settling. The mixed liquor from the aerobic reactors overflowed by gravity into the feed section of the clarifier, from which point it was distributed across the width of the rectangular clarifier vessel.

The supernatant from the clarifier overflowed via an overflow weir at the opposite end of the vessel into a collection compartment, from which it was discharged to drain.

The solids settled out in the hopper were pumped by air operated diaphragm pump back to the selector vessel where they were combined with the feed effluent and returned to the aerobic digesters (Figure 8.3). A quantity of activated sludge was periodically discharged to drain by manually opening the waste activated sludge valve (V-4002 in Figure 8.3). This sludge could be returned to the Sirolan CF feed tank, or discharged directly to drain.

8.3 RESULTS

The aims of the trials carried out with the 50,000L demonstration plant were to implement and evaluate solutions to process problems observed at the 5,000L pilot plant scale, and to investigate the continuous BOD_5 removal of a commercial scale unit under realistic operating conditions.

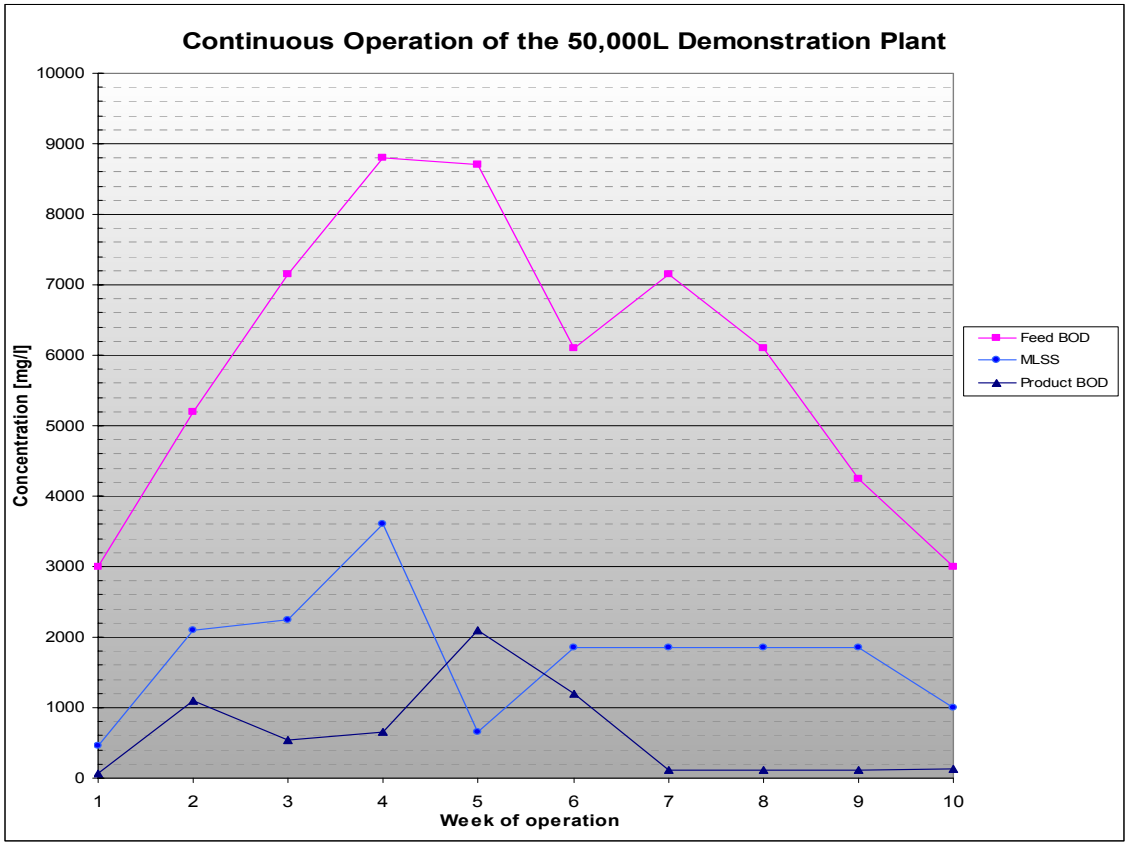


Figure 8.11 Results of the 50,000L demonstration plant trial

8.3.1 PARALLEL / SERIES OPERATION OPTIONS

All attempts to operate the plant at nominal capacity ($1m^3$/hr) with the reactor tanks in series configuration resulted in excessive caustic soda addition being required to maintain digester tank 1 in the optimum operating range of $6.5 < pH < 8.5$. Such levels of caustic soda addition would not be practicable in a commercial process. It was evident from these trials that the residence time in the first completely mixed digester must be higher than the 25 hours available under these conditions for the natural pH buffering effect of the bacterial culture to take effect.

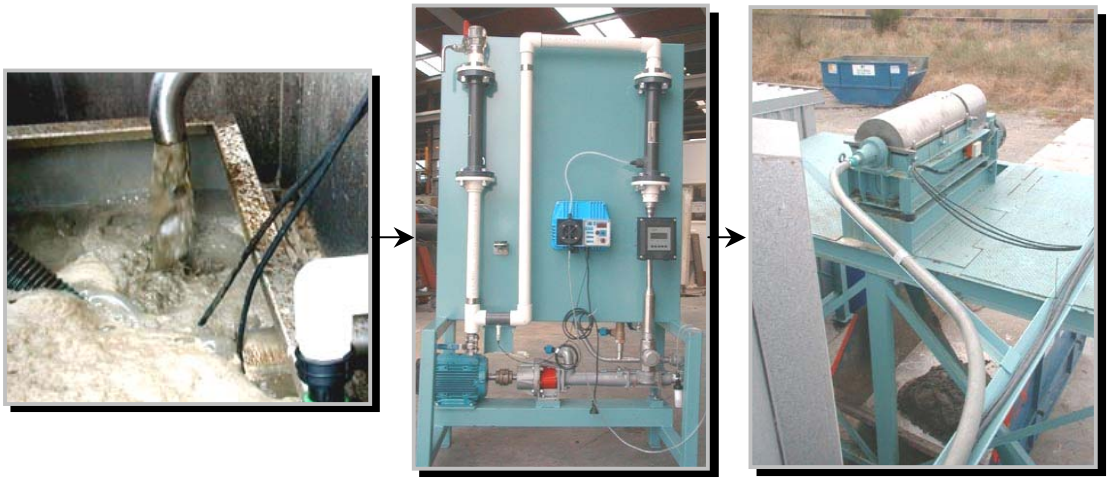
This observation supported results obtained from laboratory scale investigations in which it was shown that, for a typical strength of Sirolan CF effluent (4,000 – 8,000mg/L BOD_5), a minimum of 50 hours hydraulic residence time should be provided in the first CSTR to enable both natural buffering of the feed acidity, and sufficient BOD_5 removal to take place.

As a result of this finding, all subsequent trials carried out with the 50,000L trial reactor were performed with the two digesters operating in parallel as detailed by Figure 8.5. A minimum of 50 hours total hydraulic retention time was used.

8.3.2 CONTINUOUS OPERATION

As the 50,000L demonstration plant was to be operated in an on-line manner as would be encountered in an operational wool scour, only a small feed storage tank was included in the process design. This feed tank, equivalent to a tenth the hydraulic capacity of the combined digester vessels, was only capable of dampening the most significant flow and strength fluctuations in the feed from the scour or pre-treatment system. This vessel was also capable of providing a low level of supplementary feed to the digesters during brief periods of scour shutdown.

The key obstacle in achieving a continuous mode of operation was the reliability and effectiveness of the pilot plant chemical flocculation unit being used to supply the feed to the biological reactor (Figure 8.12).



Heavy Flow-down Effluent Tank | Sirolan CF – Acid & Polymer Addition | Decanter Centrifuge

Figure 8.12 Sirolan CF pilot plant used at Fairlie Wool Scour, Timaru Ltd

This pilot plant Sirolan CF unit (Figure 5.13, Figure 8.12) was initially designed for carrying out trials of in-line chemical flocculation at Fairlie Wool Scour, Timaru Ltd. It was never designed to be operated unattended or on a continuous basis for any length of time. This became evident as the online Sirolan CF-B testing progressed. If not constantly supervised the pre-treatment system would regularly send slugs of inadequately treated or raw wool scour effluent to the biological reactor with catastrophic consequences.

The key problems preventing continuous operation of the Sirolan CF – CF-B system and solutions implemented are outlined in Table 8.2 below:

Table 8.2 Problems encountered under continuous operation

Problem Encountered	***Solution Implemented***
The Sirolan CF acid-dosing pump was undersized and the 'proportional' pH controller unsuitable for in-line acid addition.	Pump replaced with Milton Roy, variable frequency, variable stroke diaphragm pump connected to a PID pH controller.
Gas generation during acid addition caused back-pressure fluctuations on the centrifugal effluent feed pump. This caused serious instability of both effluent flow rate and resultant effluent pH.	VF Drive controlled centrifugal effluent feed pump was replaced by a positive displacement mono-pump controlled by a PID flow control loop.
Optimum operating pH of the Sirolan CF process varied on a regular basis causing the product quality to deteriorate if a constant pH set-point was used.	A turbidity monitoring system with integrated pH control was designed and installed on the centrate line from the Sirolan CF decanter.

The most significant improvement made during this phase of the investigation was the implementation of turbidity control and monitoring of the Sirolan CF pre-treatment process as detailed in Section 5.3. Only with the inclusion of this equipment was the pilot plant Sirolan CF system able to provide consistent enough high quality feed for the biological treatment system to be run on a continuous basis.

8.3.3 FOAM CONTROL MEASURES

8.3.3.1 Reactor Design

Each of the 25,000L digestion tanks was fitted with a 1.5m tall stainless steel 'chimney' structure (Figure 8.9, Figure 8.10). The purpose of this was to determine whether, by

operating the liquid level at the base of this cylinder, the reduced surface area of liquid resulted in reduced foam generation. The extended height of the cylinder was then available to allow for foam accumulation and subsequent collapse of the foam matrix under its own weight. The height of the chimney was based on the maximum height of the foam matrix observed in the 5,000L pilot plant digester.

This approach was not successful for the following reasons:

1) The construction of the plastic tanks did not allow for any static head above the apex of the domed roof, as was required to operate the liquid level within the stainless steel chimney. This combined with weakening of the tank by inserting the air feed pipe through the centre of the roof resulted in structural failure whenever the tank was filled above these points (Figure 8.13).

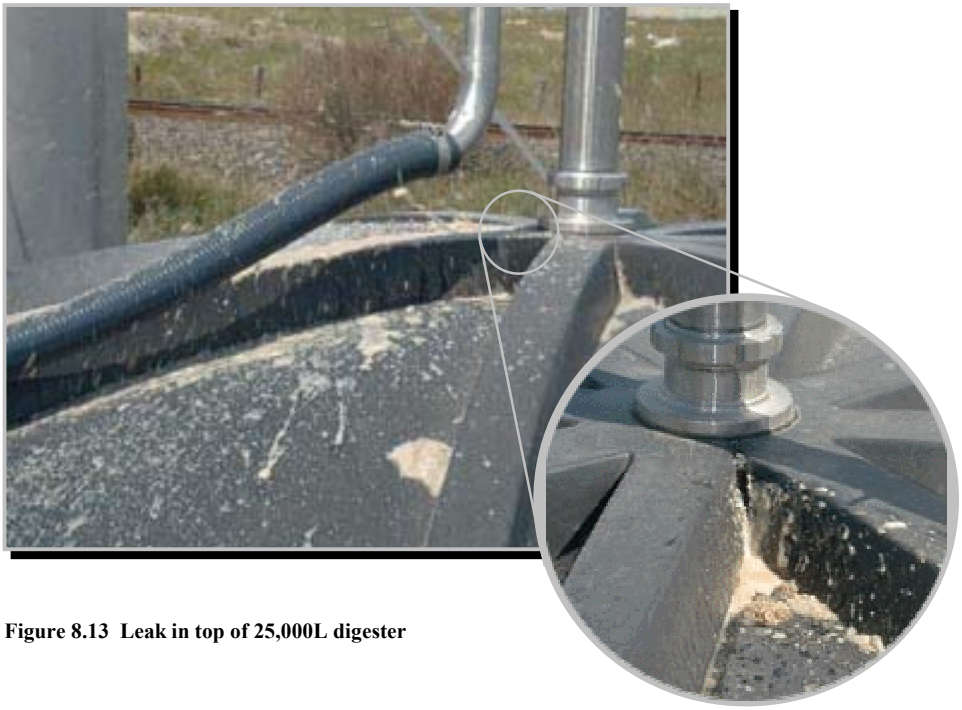


Figure 8.13 Leak in top of 25,000L digester

Even after the tanks had been repaired by plastic welding, the seams in the centre of the tank roof where the roof ribs meet (inset Figure 8.13) would re-split once pressure was reapplied to them.

2) Due to the mechanical stability of the foam, the foam matrix would 'bridge' across the width of the chimney structure. With the weight of the foam subsequently supported partially by the stainless steel walls rather than the foam itself, a greater height of foam was able to build up with the result being intermittent overflow of foam from the digester.

8.3.3.2 Spray Devices

Several spray devices were trialled in an attempt to control the production of foam in the digesters. Below is a summary of their effectiveness.

Table 8.3 Control of CF-B foam with spray devices

Spray Type	*Liquid*	*Effectiveness*
Garden Sprinkler (Large, medium velocity droplets)	Mixed liquor (From recirculation pump)	Ineffective
Hand held spray system, low velocity, small droplet size	Sirolan CF liquor pH 3.5	Ineffective
Hand held spray system, high velocity jet (0.5 – 2mm droplet size)	Sirolan CF liquor, pH 3.5 (Bioreactor feed liquor)	**Very Effective**
	Mixed liquor	Ineffective
	1 part Sirolan CF liquor : 5 parts mixed liquor	Effective
	1 part Sirolan CF liquor : 10 parts mixed liquor	Ineffective
	Cold rinse water / tap water	Ineffective
	65°C rinse water / tap water	Effective

After some time the devices that did stimulate breakdown of the foam resulted in a more condensed, heavy brown foam (or scum) accumulating on the surface of the CF-B tanks. Figure 8.14 shows new foam (centre right) swelling up through this blanket of older semi-condensed foam inside the chimney structure of one of the digester vessels.

Figure 8.14 Condensed foam inside 'chimney' of 25,000L digester vessel

8.3.3.3 Mechanical Devices

The key problem with rotating mechanical foam breakers is the high rpm required to effectively break down the foam structure (all designs tested in Section 6.3.4 were shown to be ineffective below 120rpm). In any environment where operators need access to the tank surface, these high-speed moving parts would cause a significant operator hazard.

The most practical and effective mechanical foam control device trialled was a device where the foam was drawn from the headspace of the closed-top digester into a separate cyclonic chamber (Figure 8.15), where it was broken down by a combination of centrifugal force, mechanical shear from the fan, and by the gravity head of the foam height in the chamber.

The condensed foam then flowed from the hopper-bottom of the foam destabilisation chamber, through a 2-inch hose into the feed end of the clarifier vessel. Any foam that did not collapse under the centrifugally enhanced gravity head of foam in the chamber, or shear

forces of the walls was instantly broken down upon contacting the 1450rpm centrifugal fan mounted in the top of the cyclonic chamber.

Figure 8.15 Foam destabilisation chamber

8.3.3.4 Chemical Methods

The continuous addition of a chemical anti-foam or de-foamer was considered unfavourable due to potential interaction of the chemical additive with the biological culture. The key problems expected were rapid biodegradation of the chemical requiring excessive dosing rates or bio-toxicity of the chemical leading to reduced effectiveness of the biological culture.

The two chemicals trialled were both silicon-based anti-foams suitable for use with food products for human consumption (therefore unlikely to be toxic to biological systems). These proved effective in instantly reducing the foam generation of the system at doses as low as 5 – 10 ppm in the 25,000L digester vessels.

The particular chemicals used were Silcorel AFP 20 from Reliance Silicones International, Surrey, UK, and RD Antifoam Emulsion (10% active) from Dow Corning. These antifoams are purpose designed for use in aerated bioreactors, and have approximately one-third the COD of non-silicone based defoamers such as iso-octanol, kerosene or coconut oil. The active chemical is non-toxic to biological systems and is ultimately degraded on contact with micaceous clays in the natural environment to form bio-acceptable cyclic siloxanes, which then further degrade to silica (Anderson 1997). Of these two products, the Dow RD Antifoam

proved longer acting than the Silcorel product at similar dose rates (one dosing per hour at 15ppm concentration).

8.4 DISCUSSION

8.4.1 REACTOR DESIGN

Although the use of two separate 25,000L tanks in the construction of the 50,000L demonstration plant was primarily due to the reduced cost of construction, this design also enabled the trialing of parallel and series plant operation using the two separate aeration vessels.

In trials where the two tanks were used in series, serious problems were encountered in all attempts to run the plant on a continuous basis without excessive levels of supplementary pH neutralisation. In order to obtain 50-hour residence time in the overall reactor, the first reactor to receive raw effluent had to operate with a residence time of 25 hours. In all trials this proved insufficient time for the biomass to buffer the pH of the incoming feed to a level that could support the required biological growth.

An alternative to pure series operation, which may be able to provide some of the benefits of series operation with assisted biological pH buffering from the second reactor tank, would be to operate the two tanks in series mode, as per Figure 8.4, but to include a large recycle of liquor either from the second reactor tank, or from the solids settling system.

One example of how this could be achieved without altering the overall process design would be to increase the underflow from the settler to the first reactor vessel so that the treated liquor which was recycled along with the settled sludge both diluted and neutralised the incoming feed effluent. Alternatively, a mixed liquor recycle pump could be installed on reactor 2 to recycle a given portion of the overall feed flow-back to reactor 1 – thus diluting and neutralising the mixed liquor of reactor 1 with that from reactor 2. This mode of operation would provide a compromise between series and parallel operating regimes where the equilibrium concentration of pollutants in reactor 2 was slightly lower than that in reactor 1, but the operating pH of both reactors were still maintained at levels required for healthy biomass growth. Further research would be required to establish the effectiveness of such an operating regime as this was not trialled as part of this investigation.

8.4.2 CONTINUOUS OPERATION OF THE PROCESS

The initial unreliability of the pilot plant Sirolan CF pre-treatment process used to produce the feed to the biological system was the most significant factor preventing any kind of consistent operation of the biological treatment process. Initially, if left unsupervised for as much as an hour, the pre-treatment process would often fail completely resulting in raw wool scour effluent being fed to the biological reactor – a situation that led to organic overloading of the reactor and occasionally complete reactor failure. The other problem with the pilot plant Sirolan CF unit which seriously impacted upon the operation of the biological treatment system was the unreliability of the effluent feed pump, so that the biological reactor was left without feed for as much as three days at times. The impact of these and other interruptions to the effluent feed were compounded by the lack of feed buffering volume provided in the demonstration plant design. The resultant intermittent feeding regime led to significant inconsistencies in the operation of the biological reactor, which were very likely detrimental to the effectiveness of the process.

The reliability of the pre-treatment process was considerably improved by the implementation of a turbidity monitoring and control system as detailed in Section 5.3. This system monitored the quality of the effluent from the pre-treatment process, and altered the acid dosing rate of the chemical flocculation plant to maintain optimum quality of feed to the biological reactor at all times. If the effluent being fed to the reactor ever dropped below a predetermined quality level, the turbidity control system shut down the feed to the biological reactor and sounded an audible alarm.

After all of the improvements to the pre-treatment process listed in Table 8.2 had been implemented, relatively stable operation of the biological system was obtained for a period of several weeks. This period of stable operation with the two 25,000L tanks operating in parallel yielded the results expressed in Figure 8.11.

Figure 8.11 shows that under conditions of increasing organic loading as occurred over the first four weeks of stable operation, the BOD_5 of the effluent from the biological process increased as the biomass struggled to cope with the increased organic loading. The biomass concentration in the reactors (measured as MLSS in Figure 8.11) did however eventually increase to accommodate the higher organic level in the feed. When the BOD_5 of the feed to the reactor reached a level greater than ~8,500mg/L the biomass concentration in the reactors was observed to drop suddenly, with a correspondingly sudden increase in effluent BOD_5 from 600mg/L to just over 2,000mg/L. This is consistent with observations made at

laboratory scale indicating that high concentrations of Sirolan CF liquor are toxic to the mixed culture present in the biological reactors. Reduction of the feed BOD_5 to < 7,000mg/L over the following weeks resulted in both a rapid recovery of the biomass concentration and a reduction of the effluent BOD_5 to approximately 200mg/L. This low effluent BOD_5 was maintained over the last 4 weeks of operation of the 50,000L demonstration plant. Over this time the feed BOD_5 was decreased from 7,000mg/L to 3,000mg/L, but no corresponding change was observed in the biomass concentration in the reactors until the final week when the mixed liquor suspended solids dropped from 1,800 to 1,000mg/L. The most likely explanations for this break in correlation between the biomass concentration and apparent organic loading of the reactor are:

- An undetected increase in the effluent feed rate as the BOD_5 of the effluent dropped.
- A decrease in the effectiveness (or viability) of the biomass over the three weeks where organic loading decreased and biomass concentration remained unchanged.

The first option is unlikely to be the case as the feed flow to the reactor was fitted with an electromagnetic flow meter and operated on flow control with a set-point of 1,000m^3/hr.

The second option is considered the more likely and could be due to any number of factors in the reactor becoming limiting. In particular probe drift or failure could have led to a decrease in either reactor pH or dissolved oxygen concentration which would have limited the BOD_5 removal capacity of the biomass present.

In either case, the BOD_5 of the effluent had stabilised at a level which was the lowest that had been observed from this process operating at a 50hr hydraulic residence time, so any reduction in biomass viability or effectiveness that was occurring had no effect on the overall results of the process.

8.4.3 FOAMING PROBLEMS

The demonstration plant biological reactors were designed with a number of features, particularly the foam accumulation towers in Figure 8.9 and Figure 8.10, which were intended to assist in overcoming the foam generation problems encountered at pilot plant scale. None of these design features worked as intended.

The stainless steel towers mounted on the access hatches of each tank were intended to minimise the surface area of liquid on which foam could form, while allowing height and volume for foam to accumulate and break down under its own weight. While there was indeed room for a limited amount of foam accumulation in the stainless steel towers, extensive bridging of the foam between the walls of the towers occurred, thus preventing the foam from breaking down under its own accumulated weight. The result of this was that any above average generation of foam in the reactors resulted in instant overflow of foam to the surrounding environment. The dome shaped tops of the Rotomold tanks used also prevented this design from working in that a pressurised bubble of air was trapped under the dome of the tank providing both more liquid surface for foam generation, and exerting forces on the top of the tank that were beyond its capability to withstand.

Although a range of spray systems were trialled, only spraying raw Sirolan CF liquor onto the foam reliably prevented foam accumulation. This was consistent with observations made under normal plant operation, that adding Sirolan CF liquor to a badly foaming, substrate starved reactor would instantly reduce foaming to a manageable level. A spray of dilute Sirolan CF liquor (as would be found in the selector vessel were one used) was found to be the second most effective process liquor for control of foam by spraying. In all cases high velocity, large droplet sprays were found to be the most effective at breaking down the foam.

The mechanical apparatus (detailed in Section 8.3.3.3) that was trialled for foam removal and destruction on the demonstration plant proved the most successful mechanical method of foam control. The effectiveness of this device was likely to be due, at least in part, to it being oversized for the volume of foam and air it was required to handle. As can be seen from Figure 8.15 the device consisted of a cylindrical hopper-bottomed vessel with tangential air entry near the base of the cylinder. A centrifugal fan was mounted on top of the vessel in such a way as to encourage rotation of the air inside the vessel in the same direction as the tangential air entry. Due to the high air handling capacity of the 4kW fan used, the velocity of the air / foam mixture being pulled through the feed pipes from the reactor headspace into the cyclonic chamber was high enough that most of the foam broke down from shear forces either in the pipeline or in the chamber itself. Due to the particular design constraints of this site, the foam was required to be drawn up to a height of over a metre from the reactor headspace to the inlet of the cyclonic foam destabilisation chamber. With some heavier foam types this posed a significant problem as the high flow, low pressure centrifugal fan used for drawing off the foam air mixture was unable to lift the foam to the height of the chamber so the pipe subsequently became blocked with a static plug of dense foam. In order to prevent this from occurring in the future it is strongly recommended that any such mechanical foam

handling systems use gravity to assist flow of foam downwards from the point of collection into the foam destruction chamber.

Under the most extreme conditions of foam generation, the foam level in the cyclonic foam-destabilisation chamber reached the height of the extraction fan. Upon reaching this point the foam was instantly condensed into a solids rich liquor and expelled from the fan along with the air flow. In this case a deflector plate was used at the fan outlet to contain the resultant liquid output by deflecting it into the top of the settling vessel where it was combined with the underflow from the foam destabilisation chamber. In the settler the solids were removed and the liquid from the foam matrix was allowed to overflow with the product effluent to drain.

The chemical anti-foams trialled yielded a result somewhat more economical than initially expected. Of the silicone-based antifoams trialled, the most successful option (RD Antifoam emulsion from Dow Corning) only required a few ppm to completely stop the generation of foam in the reactor tanks. It was soon discovered that it was not the concentration of anti-foam required in the tank, but rather how often the vessel required re-dosing that was the critical factor in determining the daily use of the chemical. While only a very small dose of anti-foam was required to stop the foaming altogether, this same quantity had to be re-dosed anywhere from once per hour to once per 5 hours to prevent excessive foam generation from re-commencing.

Silicone based antifoams are preferred to other organic products such as iso-octanol or kerosene as silicones are chemically inert and do not affect the metabolism of micro-organisms. Although dimethylpolysiloxane (the active ingredient used in silicone antifoams) is highly resistant to biological degradation, and is therefore not affected by the biological process, it does undergo natural chemical degradation to silica upon contact with micaceous clays in the natural environment. This minimises any potential environmental impact of dosing this chemical into effluent that is later discharged to natural waterways. Based on economics and effectiveness of this method, the decision was made to fit all future reactors with antifoam dosing systems.

9 FINAL PROCESS DESIGN

As a result of the investigations carried out to this point, final process design of a commercial scale biological treatment system for the reduction of BOD_5 loading in heavy wool scouring effluent pre-treated by the Sirolan CF process was developed in co-operation with ADM Group Ltd, Timaru. The process has been titled Sirolan CF-B after the pre-treatment process 'Sirolan CF' developed by the Australian CSIRO Division of Textile and Fibre Technology. The '-B' suffix indicates this as the biological component of the integrated treatment package.

9.1 REACTOR TYPE

The overall type of reactor determined to be the optimum configuration for the degradation of wool scour effluent treated by the Sirolan CF process, was a continuously stirred tank reactor (CSTR) with hydraulic residence time of no less than 50 hours.

Due to practical considerations the final reactor was constructed as two 50 hour hydraulic residence time digestion basins operating in parallel. The duplication of aeration and recirculation systems in these two basins gave a level of redundancy as a contingency against failure of one of these systems. The process is designed such that one basin could be emptied for maintenance while the entire effluent flow is diverted through the other digester basin.

9.2 TURBIDITY CONTROL

The inclusion of feed turbidity monitoring and control as detailed in Section 5.3 was made mandatory on all applications where this plant was to process effluent pre-treated by the Sirolan CF process. This system ensured that the effluent met a predetermined level of treatment before being allowed to enter the biological system. If the feed effluent failed to meet the required standard, it was automatically diverted back to the feed of the pre-treatment system for reprocessing and an operator alarm was sounded.

9.3 SELECTOR ZONE

Although the feed effluent has been confirmed to be non-readily degradable (Section 6.4.1) an anoxic selector zone was included prior to the reactor basin, where the return activated sludge

is contacted with a high concentration of feed effluent in the presence of mixed liquor dilution water which maintains the pH in an acceptable range for the growth of non-filamentous bacteria. This initial contact with a high concentration of effluent promotes the growth of non-filamentous bacteria in the digester basin, thus improving both the settling characteristics and reducing the foaming potential of the biomass.

The inclusion of this anoxic selector zone with built-in mixed liquor recycle gives the treatment system an extra potential nitrification – de-nitrification capacity, possibly useful in the future, especially if nutrient discharge levels are tightened as is commonly occurring throughout the world.

For promotion of the growth of non-filamentous bacteria, Eckenfelder (Eckenfelder 1989) recommends that the retention time in the selector zone be of the order of 15 minutes to maximise bio-sorption of the substrate into the biological flocs. This is a phenomenon where a large portion of the substrate is removed from the liquid phase in the initial minutes of contact with the mixed activated sludge. Rather than being metabolised by the micro-organisms, in this initial phase the substrate is primarily removed by physical adsorption onto the biological sludge. (Eckenfelder 1992)

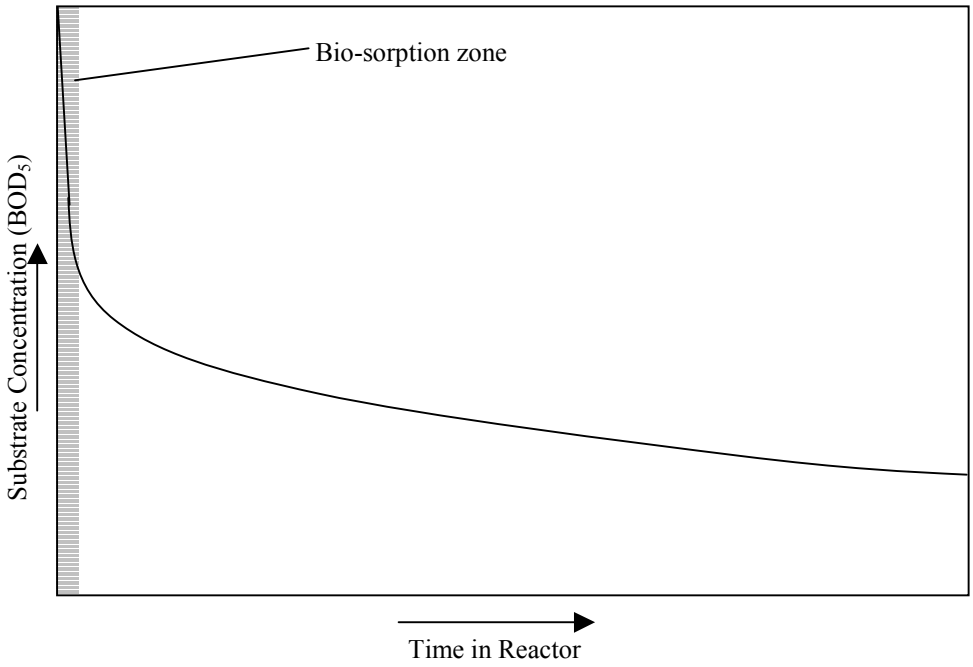


Figure 9.1 Substrate uptake in a complete mix reactor

By carrying out this bio-sorption phase in a separate contacting / selector vessel prior to the main digestion tank, the concentration gradient driving mass transfer of substrate from the

liquid phase into the biological floc matrix is maximised, thus minimising the substrate loading that remains to be removed from the liquor in the main digestion vessel.

The extreme application of this technology is embodied in the contact - stabilisation process. In this application the feed effluent is contacted with a high concentration of activated sludge for a period of typically 15 – 60 minutes, during which up to 95% of the soluble substrate is adsorbed into the sludge matrix. The liquid product and substrate-laden sludge are then separated in a gravity clarifier and the treated liquid is discharged. The recycled activated sludge is aerated for typically 2 – 8 hours in a stabilisation basin to degrade the adsorbed substrate before being returned to the contact basin for further adsorption of feed substrate.

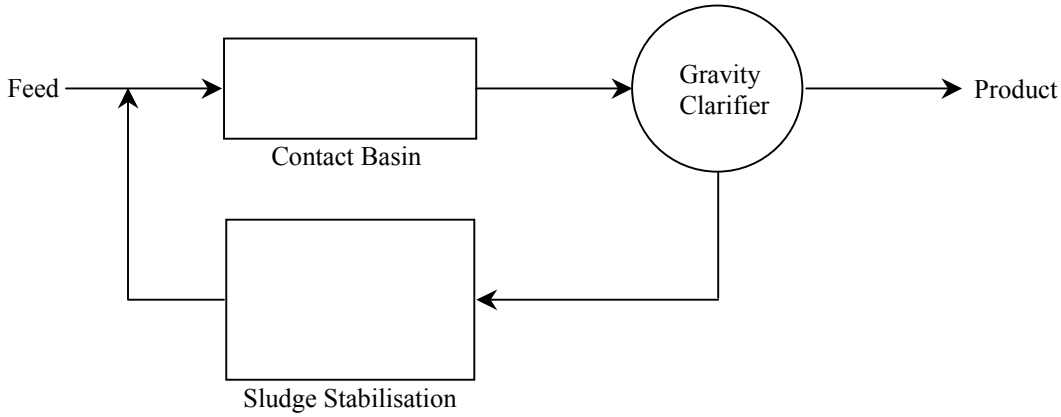


Figure 9.2 Contact Stabilisation process

This process is most applicable to readily degradable effluents such as municipal sewerage, and typically operates free of bulking and other sludge quality problems (Eckenfelder 1989). If the pre-treatment of wool scouring effluents was improved sufficiently to make the waste classifiable as 'readily degradable' (such as by improved removal of wool wax and nonyl-phenol detergents prior to biological processing) then this type of process would potentially be capable of treating the effluent to the same level with a much reduced reactor volume required.

9.4 DIGESTION BASINS

The 250m^3 digestion basins used in the final process design were each 5m x 10m in area and 5m deep with a sump for a submersible recirculation pump. The liquor from the selector vessel overflowed by gravity into each digester, thus ensuring equal distribution of feed

between the two digesters. The product stream from each digestion vessel then overflowed by gravity into the clarifier vessel.

As detailed by the piping and valve layout in Figure 9.3, the inlet and / or outlet to either digester could be closed, and the two digester vessels could be connected, thus allowing any combination of series, parallel, or 'series with recycle' modes of operation to be utilised.

It must be noted that if the digestion basins are to be constructed from concrete, then either specific SR-type concrete must be used to withstand the level of sulphate present in the effluent or the basins must be lined with a sulphate resistant coating such as fibreglass. The sulphate concentration of effluent pre-treated by the Sirolan CF process was found to typically be 9,000 – 12,000mg/L. The relevant concrete specification is covered by New Zealand Standard NZF3122, 1995 (Standards New Zealand 1995).

9.5 AERATION SYSTEM

Based on a maximum allowable influent COD of 36,000mg/L, and a maximum average effluent flow rate of $7m^3$/hr for the $5m^3$/hr nominal capacity plant, a blower capacity of $3{,}000Nm^3$/hr was calculated. This calculation utilises the standard oxygen transfer capacity of 17 $g_{O_2}/Nm^3_{air}/m_{basin\ depth}$ given by Korting AG, Germany for the aeration devices used (Korting 1999) to give 255kg/hr of oxygen transfer for the maximum allowable influent loading as outlined above of 252kg/hr of COD. To deliver this capacity of air at the static head of the injectors (5m below the liquor surface) a 55kW SVR 220 positive displacement blower by Windsor Engineering Group Ltd, Wellington was used. The blower was pulley driven and a range of pulleys was supplied to allow the blower to be run at 100%, 75% or 50% of total capacity. The compressed air stream was fed through a common manifold to the aeration basins at which point this manifold split into four air feed lines, one to each aerator (as per Figure 9.3).

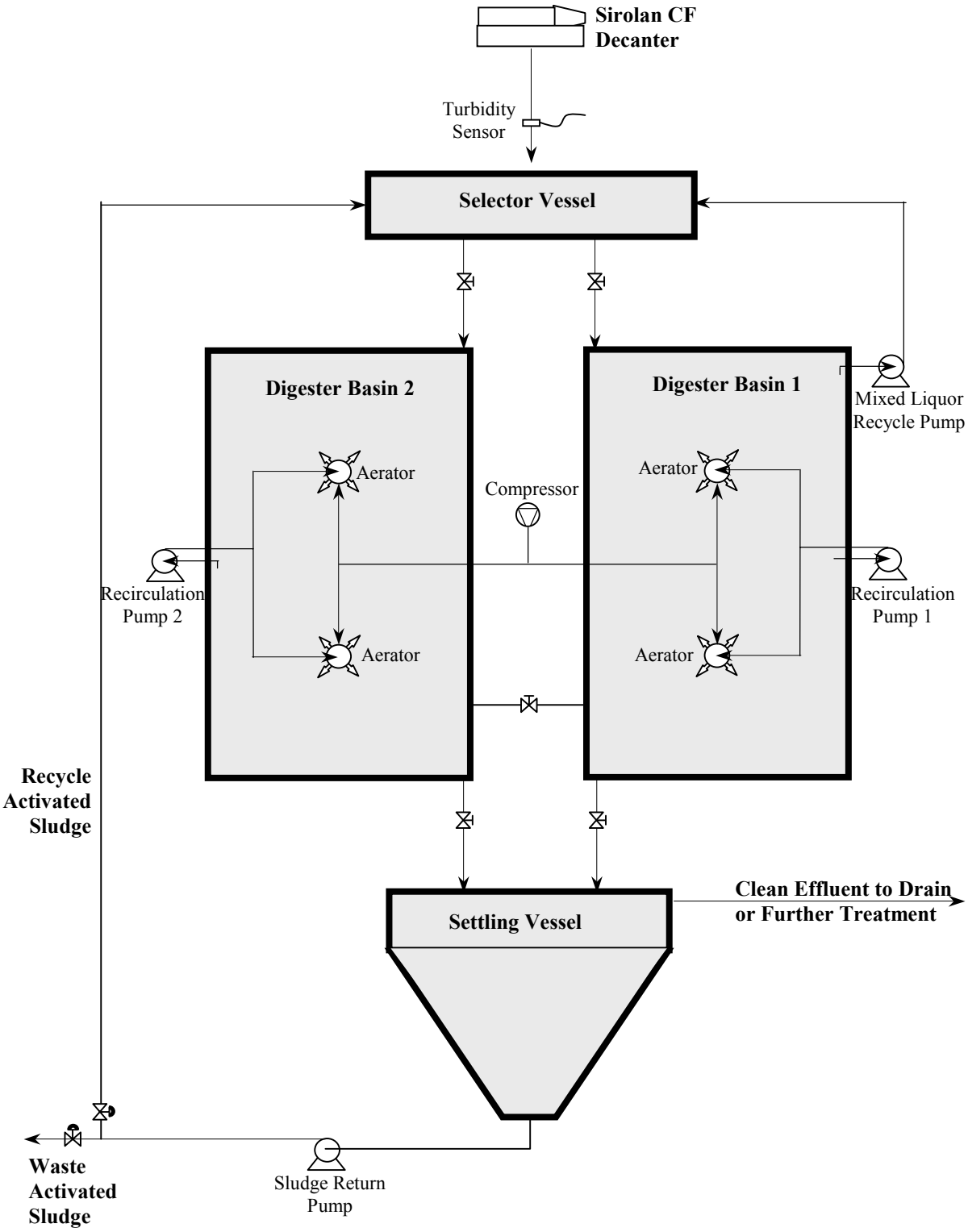


Figure 9.3 Process flow diagram of final reactor design

The aerators used were of the 9-path venturi injection type as supplied by Korting Hannover AG (Figure 8.7). To achieve optimum mixing and oxygen transfer to the bulk liquid, two

aerators were installed in each digester basin. The two aerators in each basin were supplied with motive effluent flow by a common recirculation pump (Figure 9.3).

The motive flow for the aeration system was supplied by two Zenit 2500/4/150 submersible recirculation pumps (Figure 9.4), each capable of supplying 360m^3/hr of motive flow (180m^3/hr per aerator) at 11.6 m head.

These pumps were installed submersed in a sump in the base of each digester basin as shown in Figure 9.5. The pumps were mounted on hoisting rails, so that they could be removed for maintenance without having to empty the vessel.

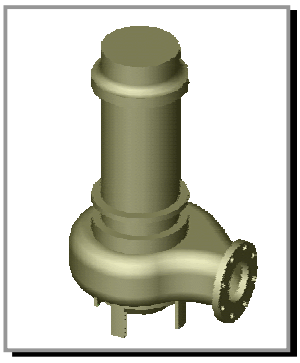


Figure 9.4 Zenit submersible recirculation pump used in final reactor design.

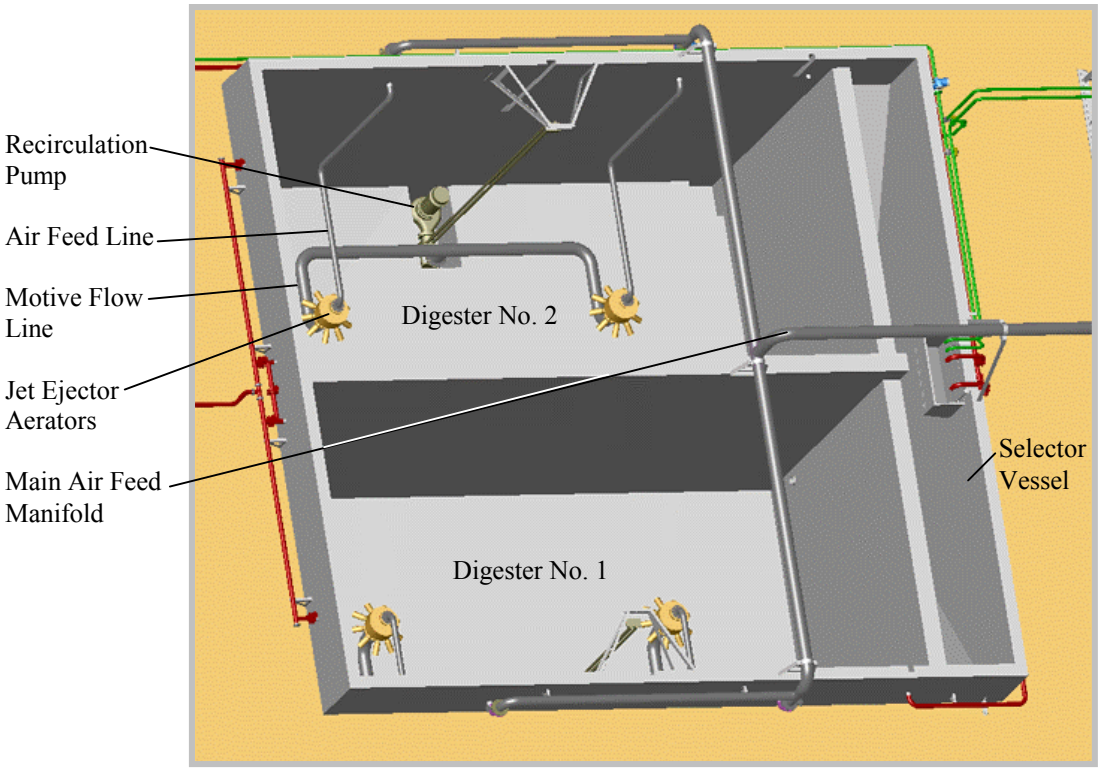


Figure 9.5 Aeration system layout in digester vessels – overhead view of empty vessels

Each recirculation pump was run by a 25kW Variable Frequency (VF) Drive, thus allowing the recirculation rate to be reduced to the minimum level required to achieve sufficient oxygen transfer to the aqueous phase. The reactor system was fitted with dissolved oxygen

monitoring, and the option has been made available to operate the recirculation pumps as part of a dissolved oxygen control loop with the Process Logic Controller (PLC) increasing or decreasing the speed of the recirculation pumps in order to achieve a given dissolved oxygen set-point in the digester basins.

Although this is not the recommended method of controlling oxygen transfer rate with venturi-jet ejectors (Meyer 2001), it was found at pilot plant level that reducing the motive flow rate while maintaining a consistent air flow to the injectors produced larger air bubbles. While this results in lower oxygen transfer efficiency, it also results in significantly reduced foaming in the digestion vessels. Foaming in the digestion vessels is one of the key outstanding issues with the process design for this type of reactor system.

9.6 SOLIDS SETTLING SYSTEM

The solids settling system used in this design was an in-ground, rectangular, hopper-bottomed gravity clarifier / thickener. This unit was designed for a maximum overflow rate of $10m^3/hr$, which is equivalent to $0.4m^3/hr$ per m^2 of clarifier surface area in the 5m x 5m vessel. This value is conservative by comparison to the Water Environment Federation (WEF) guidelines which suggest allowing for an average overflow rate of 0.5 – 1.0 $m^3/m^2.hr$ in municipal treatment systems operating at a similar level of MLSS (Water Environment Federation 1998).

The general construction of the clarifier vessel is shown in Figure 9.6. This tank was then fitted with a stainless steel perforated baffle at the feed end to ensure even flow distribution of the feed over the entire available area of the vessel. The feed zone defined by this baffle also acted as an energy dissipation and flocculation chamber in which floc growth was promoted by the initial turbulence of the feed entry (Figure 9.7, Figure 9.8).

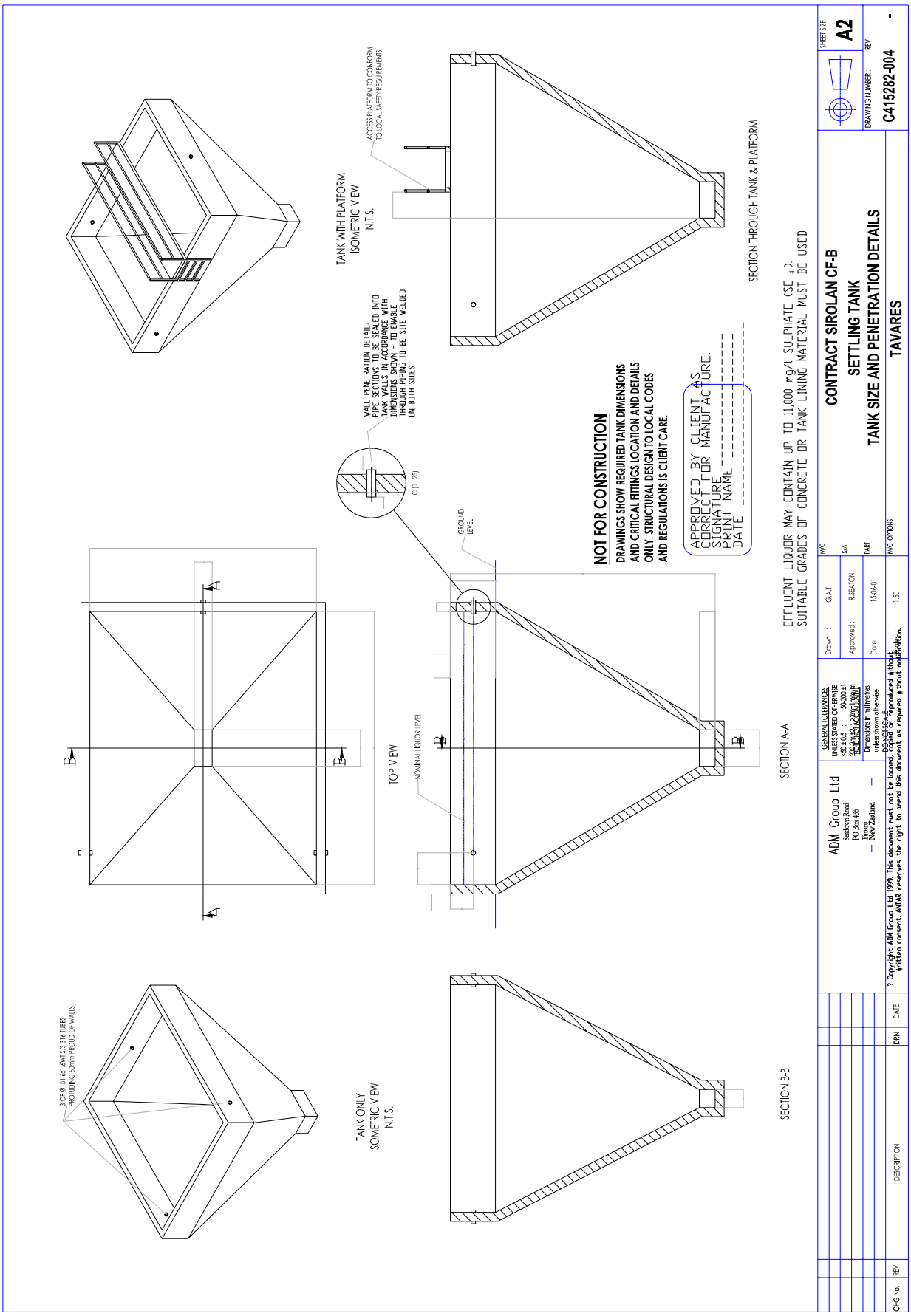


Figure 9.6 Design of gravity clarifier for commercial biological reactor system (Reproduced by permission – ADM Group Ltd.)

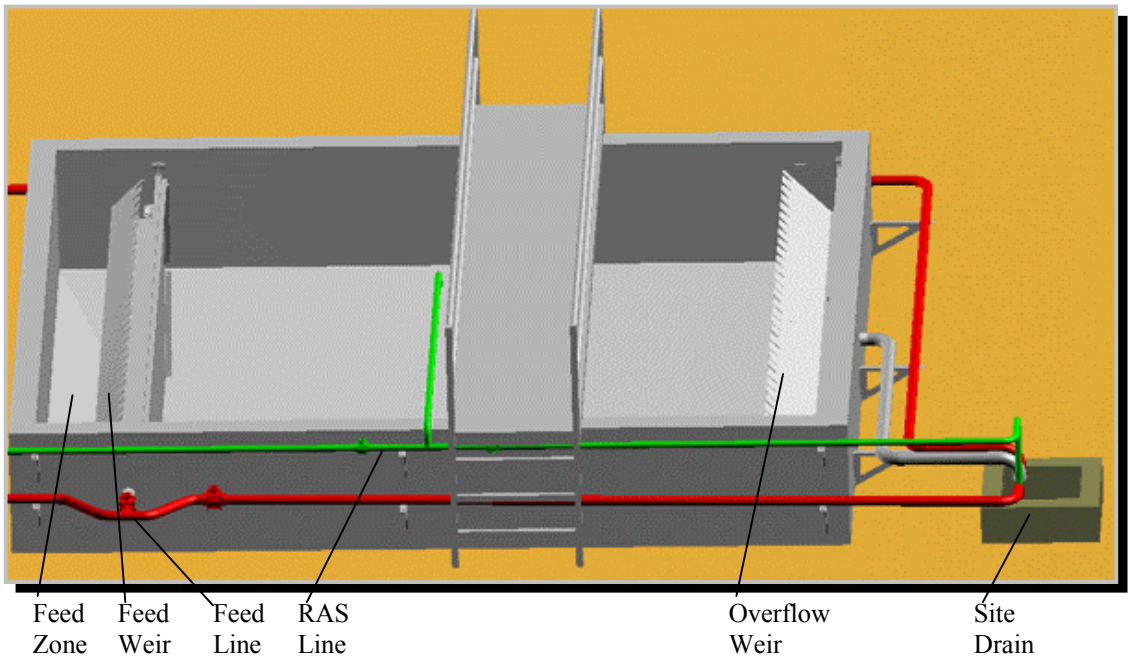


Figure 9.7 Gravity clarifier with inlet and outlet assemblies installed (Reproduced by permission – ADM Group Ltd.)

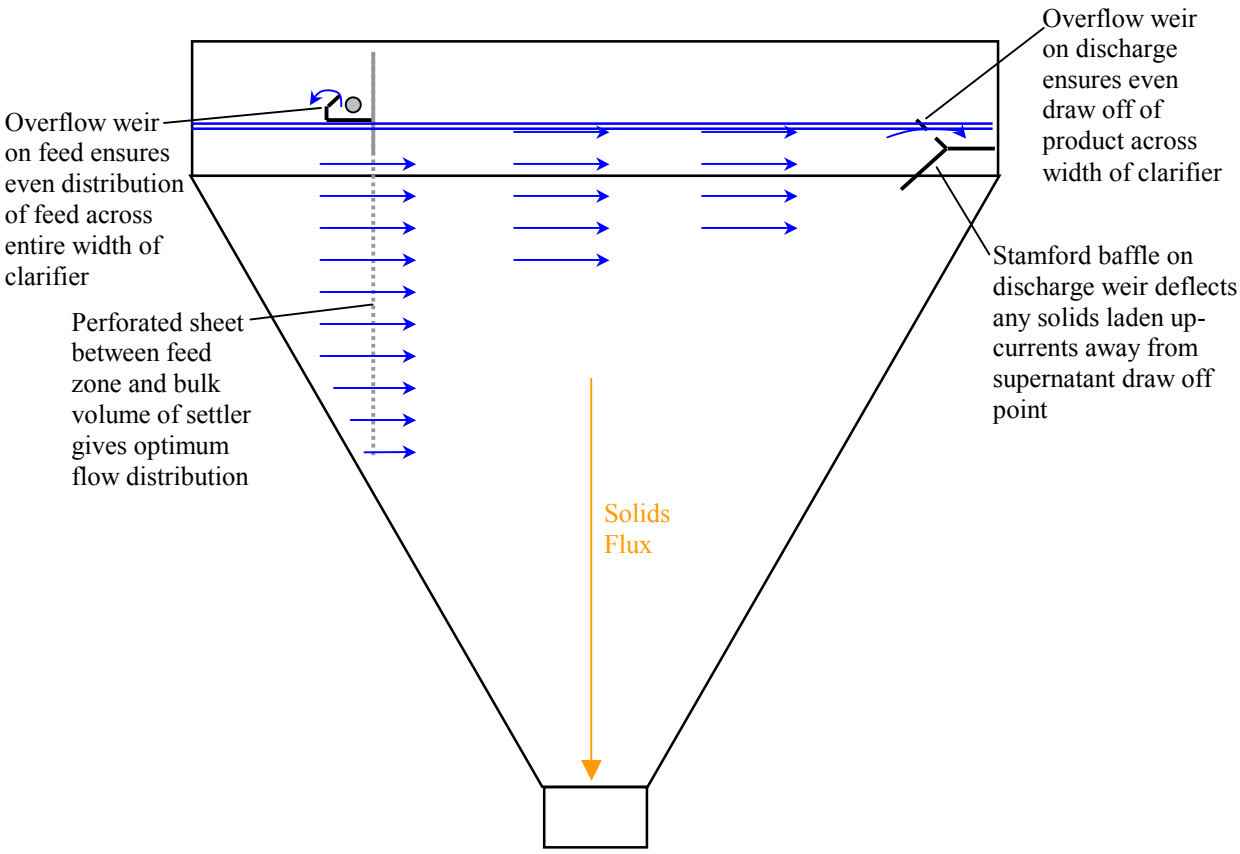


Figure 9.8 Liquor flows and function of internal structure of gravity clarifier

A three dimensional computational fluid dynamic model of the clarifier was used to model the liquor flows and detect any potential recirculation currents or short-circuiting that may occur under the expected operating conditions.

The results given in Figure 9.9 and Figure 9.10 illustrate the flow distribution in the clarifier when operating under the most extreme conditions expected in normal operation. The flow parameters used in this model were:

Inlet flow: $19m^3$/hr through the perforated plate represented by the vertical right hand wall in Figure 9.9 and Figure 9.10.

Solids draw-off: $9m^3$/hr of Return Activated Sludge (RAS) drawn off from the base of the clarifier hopper. (The bottom of Figure 9.9)

Product overflow: $10m^3$/hr of supernatant overflowing the outlet weir - represented by a 10cm deep slot across the top of the left hand wall in Figure 9.9.

As illustrated in Figure 9.10 on the following page, there was no significant short-circuiting predicted across the surface of the tank. Similarly, Figure 9.9 illustrates a distinct lack of recirculation flow and macro-eddies in the vertical profile of the tank.

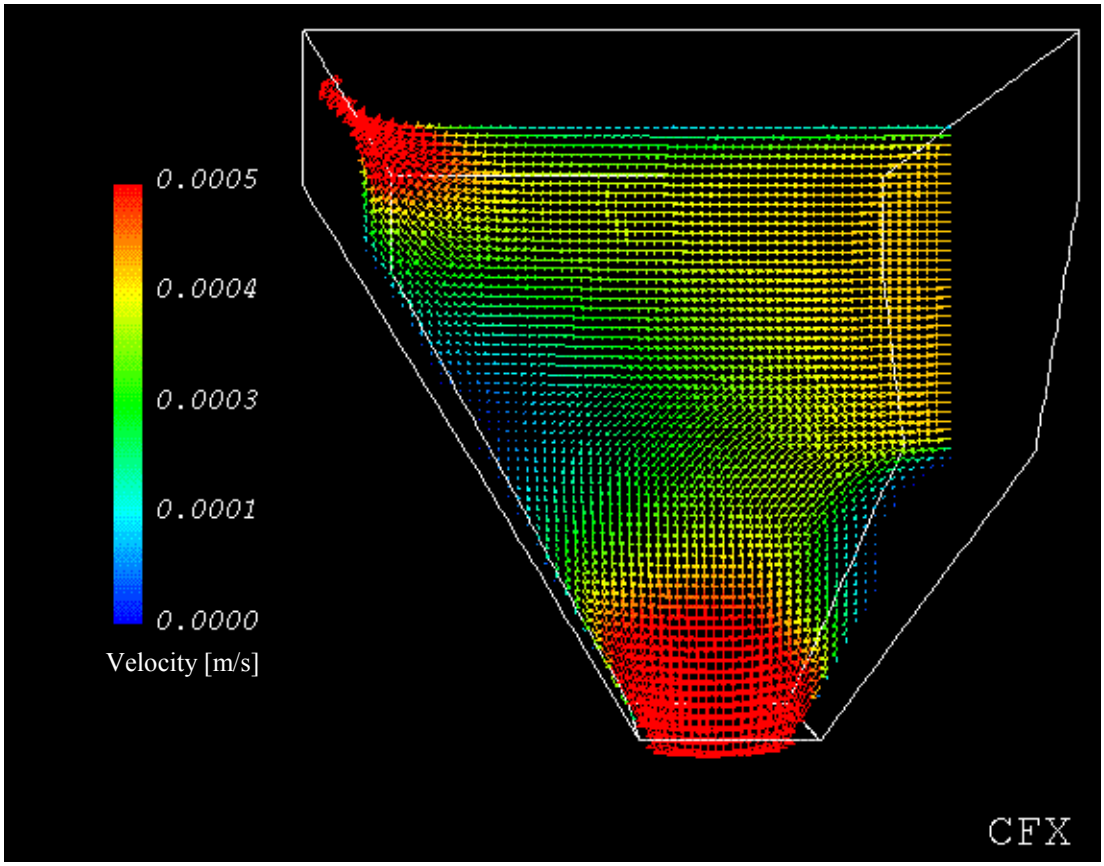


Figure 9.9 Flow distribution over a vertical slice of the clarifier vessel

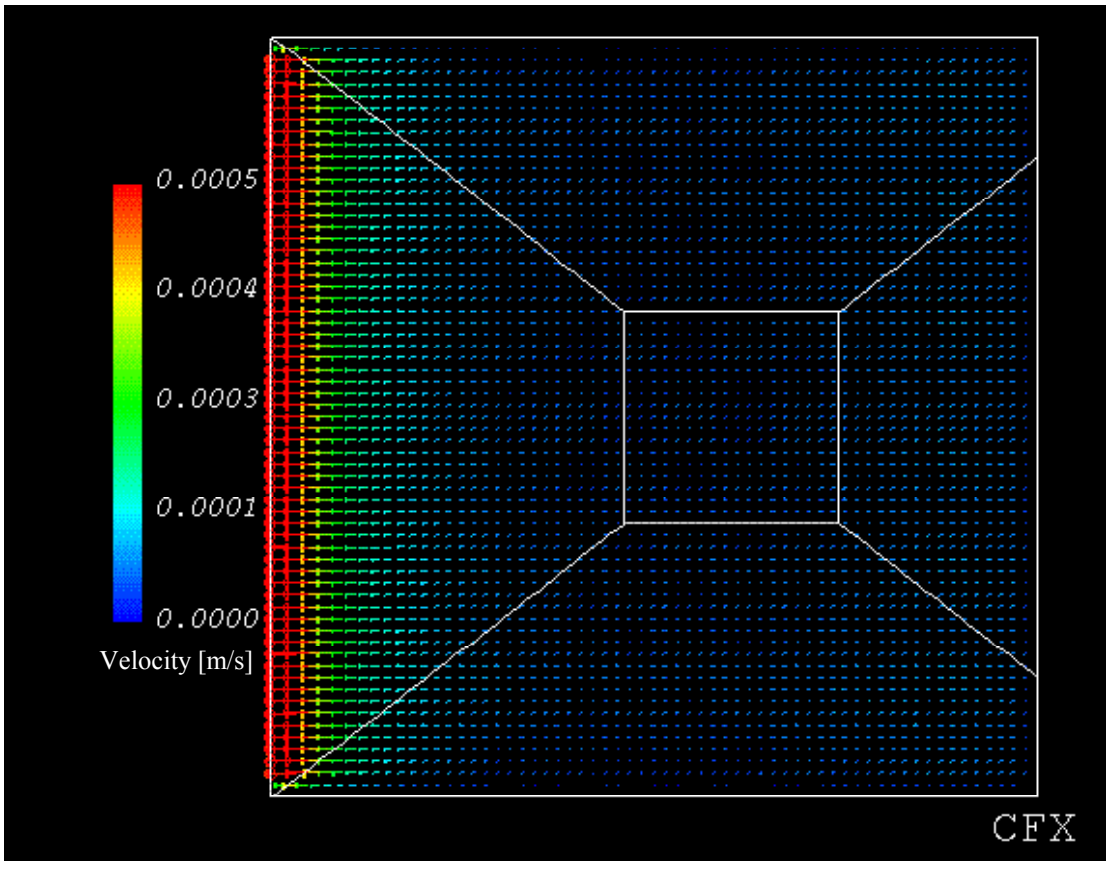


Figure 9.10 Flow distribution over a horizontal slice 5cm below liquor surface of clarifier vessel

Recycled Activated Sludge (RAS) was removed from the settling vessel by a stainless steel Zenit DRX 150/2/G50T submersible sump pump located in the sump in the bottom of the clarifier hopper (Figure 9.6, Figure 9.8). This pump was specified to supply up to $10m^3$/hr of recycled sludge to 14m head at as much as $25\%_{w/w}$ solids loading.

Under normal operation this sludge would be pumped back to the selector vessel to increase the active biomass concentration in the digester vessels. Periodically a portion of the recycled sludge is wasted in order to maintain an acceptable sludge age and food / micro-organism (F/M) ratio in the digesters (Figure 9.3). This Waste Activated Sludge (WAS) is pumped back to the feed of the Sirolan CF system where it is removed along with the solids fraction of the raw wool scour effluent. The fraction of sludge wasted is determined by the operators and entered into the process PLC, which automatically diverts the recycled sludge to the waste line on a timed basis.

A key parameter to be used when determining what proportion of sludge to waste is sludge age, also known as sludge retention time.

Sludge age can be defined as the average amount of time any given bacterial floc spends in the digestion system before it is discarded as Waste Activated Sludge (WAS). Due to the sludge recycle used in the biological process the Sludge Retention Time (SRT) in the reactor is generally significantly higher than the Hydraulic Retention Time (HRT).

Orhon and Artan (Orhon *et al.* 1994) give the following correlation for Sludge Retention Time:

$$SRT = \frac{VX}{(Q - Q_W)X_e + Q_W X_r}$$

Where SRT = Sludge retention time (or sludge age) [days]
V = Volume of the reactor [m^3]
X = Mixed liquor suspended solids [mg/L]
Q = Volumetric feed rate [m^3/hr]
Q_w = Sludge volume wasted [m^3]
X_e = Suspended solids concentration of the clarified effluent [mg/L]
X_r = Suspended solids concentration in the recycled sludge [mg/L]

In order to allow acclimatisation of the micro-organisms to the toxic and bio-inhibitory components of the feed effluent, particularly nonylphenol ethoxylate detergent, a sludge age of at least 20 days is recommended (Figure 9.11, Eckenfelder 1992). In a 7m^3/hr Sirolan CF-B plant this correlates to 0.2 – 1m^3/day of activated sludge wastage.

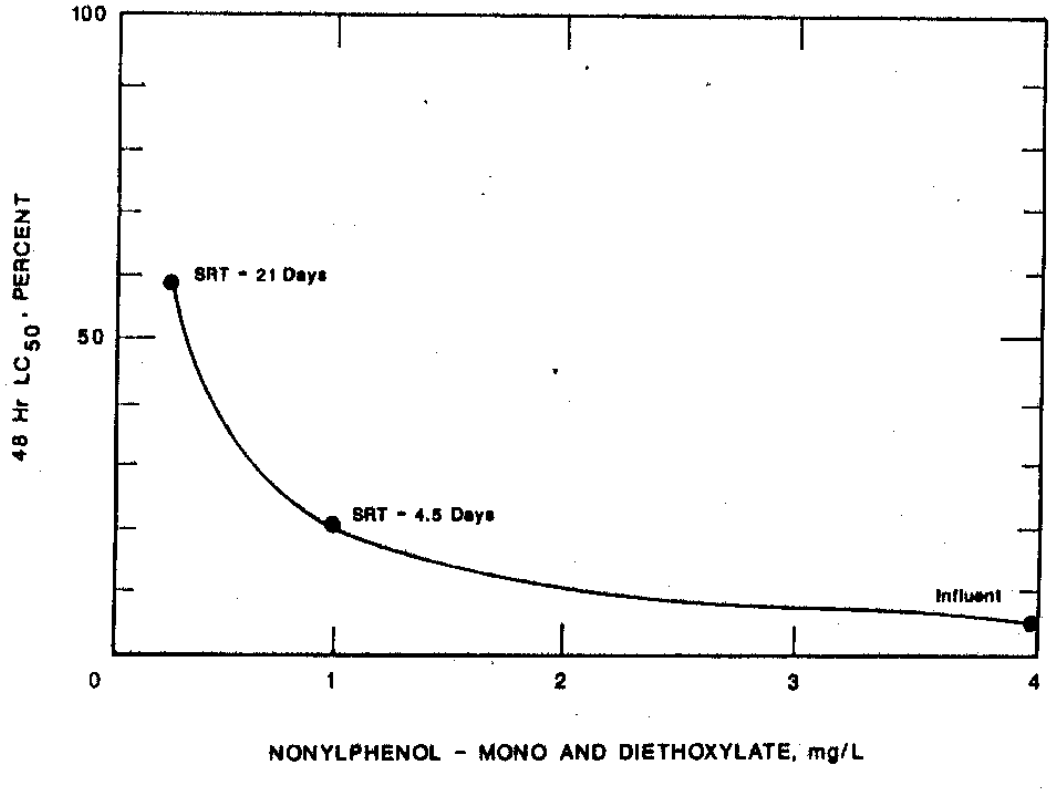


Figure 9.11 Nonylphenol ethoxylate toxicity to microbial cultures

In Figure 9.11 the y-axis units of LC_{50} %, is proportional to the concentration of toxin that is lethal to 50% of the biological population. This represents decreasing toxicity of the effluent, as the higher the LC_{50} concentration, the less toxic the substance. It can therefore be determined by this chart that increasing the sludge age (or SRT) in the biological reactor decreases the concentration of nonylphenol ethoxylate and subsequent toxicity of the combined effluent. This is of utmost significance to this treatment process as the product from the chemical flocculation pre-treatment of raw wool scouring effluent fed to the biological reactor typically contains 60 – 80mg/L of Nonylphenol ethoxylate (Jones *et al.* 1999) as opposed to the 4mg/L given as highly toxic in the example by Eckenfelder in Figure 9.11. (Eckenfelder 1992)

High sludge retention times (20 days or more) are also reported to be conducive to the growth of denitrifying bacteria in the anoxic zones of the reactor. Eckenfelder (Eckenfelder 1989) observes that for effective nitrification (and subsequent de-nitrification) to occur, the sludge age must be greater than the reciprocal of the growth rate of *Nitrosomonas* bacteria. Eckenfelder goes on to give the following correlation for the critical sludge age for nitrification:

$$SRT = 2.13e^{0.098(15-T)}$$

where T = the reactor temperature in °C

Subsequently for a typical reactor operating on wool scouring effluent, if nitrification – denitrification is to be optimised, the sludge retention time should be maintained at a level greater than:

$$SRT = 2.13\ e^{0.098(15-25°C)}\ \text{[days]}$$

$$SRT = 0.8 \text{ days}$$

which is significantly less than the sludge retention time required for acclimatisation of the micro-organisms to the toxic substances present in this particular effluent stream, and should therefore not be limiting.

9.7 ECONOMIC ANALYSIS

9.7.1 CAPITAL COST

Due to the commercial nature of this research, including an economic breakdown of the final reactor design in open literature would be unwise. This section however details the overall capital and operating cost of the process, along with the potential savings this represents in various locations around the world.

Table 9.1 Approximate capital cost of Sirolan CF / Sirolan CF-B effluent treatment system ($NZ, 2002)

	5m^3/hr Capacity	**10m^3/hr Capacity**	**20m^3/hr Capacity**
Sirolan CF Plant	NZ$225,000	NZ$250,000	NZ$250,000
Sirolan CF Decanter	NZ$150,000	NZ$150,000	NZ$250,000
Sirolan CF Total	NZ$375,000	NZ$400,000	NZ$500,000
Sirolan CF-B Plant	NZ$500,000	NZ$500,000	NZ$600,000
Sirolan CF-B Civil Works and Tanks	NZ$500,000	NZ$800,000	NZ$1,200,000
Sirolan CF-B Total	NZ$1,000,000	NZ$1,300,000	NZ$1,800,000
Combined Total	1,375,000	1,700,000	2,300,000

Note: Construction cost of the Sirolan CF-B tanks is highly site specific based on local earth and seismic conditions and the subsequent tank design required. The costs given in Table 9.1 are typical values for moderate seismic conditions and a deep water table, and may vary by as much as ± 50% in other locations.

9.7.2 COST OF EFFLUENT DISCHARGE

New Zealand

The trade waste charges in New Zealand vary widely from region to region. The trade waste charges given in Table 9.2 are for an urban centre in New Zealand, which shall not be named to prevent identification of the wool scour, to which these charges apply.

Table 9.2 Trade waste discharge cost for an urban centre in New Zealand

Flow Charge	0.238	NZ$ / m^3
Suspended Solids Charge	0.452	NZ$ / kg_{SS}
COD Charge	0.199	NZ$ / kg_{COD}

Australia

In one Australian urban centre where wool scouring takes place the following charges are imposed on effluent discharge to sewer. Again the location of the scour in question shall not be divulged due to the commercial sensitivity of this information.

Table 9.3 Trade waste costs of an Australian wool scour

Flow Charge	0.33	A$ / m^3
Suspended Solids Charge	0.17	A$ / kg_{SS}
BOD_5 Charge	0.36	A$ / kg_{BOD}

United Kingdom

In a UK urban centre where wool scouring currently takes place, the following charges are imposed on discharge of trade waste to sewer:

Table 9.4 Trade waste costs of a UK wool scour

Flow Charge	0.68	£ / m^3
Suspended Solids Charge	0.701	£ / kg_{SS}
COD Charge	0.772	£ / kg_{COD}

An average wool scour across these regions will produce heavy flow-down effluent with the following characteristics:

Table 9.5 Average heavy flow-down characteristics from a wool scour

Component	No Treatment	Sirolan CF treatment only	Sirolan CF + CF-B treatment
Volume Flow	8.0 m^3/hr	8.0 m^3/hr	8.0 m^3/hr
Biological Oxygen Demand BOD_5	32,000 mg/L	4,000 mg/L	500 mg/L
Chemical Oxygen Demand COD	96,000 mg/L	12,000 mg/L	4,000 mg/L
Total Suspended Solids TSS	50,000 mg/L	600 mg/L	600 mg/L

9.7.3 OPERATING COST

The operating cost of Sirolan CF and CF-B is highly dependent on the local cost of chemicals, sludge disposal and electricity. Average costs for the each country are given in Table 9.6

Table 9.6 Average operating cost of the treatment processes

Cost Component	New Zealand	Australia	United Kingdom
CF Chemical Cost	NZ$5.00 / $m^3_{effluent}$	A$ 3.69 / $m^3_{effluent}$	£ 0.76 / $m^3_{effluent}$
CF-B Electricity Cost	NZ$0.30 / $m^3_{effluent}$	A$ 0.66 / $m^3_{effluent}$	£ 1.67 / $m^3_{effluent}$
Total	NZ$5.30 / $m^3_{effluent}$	A$ 4.35 / $m^3_{effluent}$	£ 2.43 / $m^3_{effluent}$

Based on Table 9.2 to Table 9.6, the net annual cost of operating each option can be determined as shown in Table 9.7 to Table 9.9.

9.7.4 ANNUAL COST OF TREATMENT

The following tables illustrate the cost of effluent disposal in each of the countries in question. The annualised capital cost of the treatment process is not included in the resultant total effluent disposal cost so that these results can be used to illustrate the payback period of each treatment option. The electricity and chemical costs as given in Table 9.6, and effluent discharge fees in Table 9.2 to Table 9.4 are taken from an operational wool scour in each country at the time of publishing. These values are not necessarily representative of the corresponding costs elsewhere in each country.

Table 9.7 Economic analysis of effluent treatment options for a New Zealand wool scour (all costs in $NZ)

	No Treatment	**Sirolan CF only**	**Sirolan CF & CF-B**
Total Effluent Discharge Cost	$ 2,013,000	$ 139,000	$ 62,600
Operating Cost of Effluent Treatment Plant	$ 0	$ 240,000	$ 254,000
Total Annual cost of Effluent Disposal	**$ 2,013,000**	**$ 379,000**	**$ 316,600**

Table 9.8 Economic analysis of effluent treatment options for an Australian wool scour (all costs in $Aus)

	No Treatment	**Sirolan CF only**	**Sirolan CF & CF-B**
Total Effluent Discharge Cost	$ 976,800	$ 89,900	$ 29,400
Operating Cost of Effluent Treatment Plant	$ 0	$ 177,100	$ 208,800
Total Annual cost of Effluent Disposal	**$ 976,800**	**$ 267,000**	**$ 238,200**

Table 9.9 Economic analysis of effluent treatment options for a UK wool scour

	No Treatment	**Sirolan CF only**	**Sirolan CF & CF-B**
Total Effluent Discharge Cost	£ 5,272,400	£ 497,500	£ 201,100
Operating Cost of Effluent Treatment Plant	£ 0	£ 36,500	£ 116,600
Total Annual cost of Effluent Disposal	**£ 5,272,400**	**£ 534,000**	**£ 317,700**

It can be seen from the results of Table 9.7 to Table 9.9 that the payback on installing the Sirolan CF process for treatment of the primary effluent is extremely short. The payback based on the capital costs given in Table 9.1 is an incredible one and a half weeks in the case of the UK scour (at which site it is actually not economically possible to operate the scour with raw wool scour effluent being discharged to drain), and just over three months for the worst case, the Australian scour.

Although the overall cost of installing the Sirolan CF-B biological treatment process is higher for a scour that is already operating the Sirolan CF process (2 year payback in the UK case, and an approximately 35 year payback in the Australian case) the reason for installing this

technology is not generally to reduce the cost of effluent discharge, but to lower the effluent strength to the point where discharge consents can be met. The economic advantage of installing the biological treatment process is therefore not necessarily gained directly from reduced effluent disposal costs, but rather from the ability to continue operating the scouring process under ever tightening effluent discharge limitations.

10 RECOMMENDATIONS FOR FUTURE RESEARCH

Isolation and quantification of bio-inhibitory fractions of the Sirolan CF effluent stream

- Verification of nonylphenol ethoxylate toxicity effect
- Influence of wool grease concentration

Component analysis of Sirolan CF effluent stream

- Identification and removal of colour-contributing components
- Identification of bio-refractory fraction

Evaluation of methane production and wool grease separation in a low hydraulic residence time anaerobic reactor processing raw wool scouring effluent.

Investigation of effect of shear forces and mixing rate in the aerobic reactor on sludge settling in an activated sludge process treating chemically flocculated wool scouring effluent.

Quantification of kinetics of bicarbonate production and acid neutralisation in the Sirolan CF-B activated sludge process.

Evaluation of a wide range of chemical anti-foams for the prevention of excess foam generation in the Sirolan CF-B process.

Long term sludge quality monitoring of the Sirolan CF-B activated sludge process operating at Kaputone Wool Scour, Christchurch.

Evaluation of advanced solids separation systems – membranes and porous media – for biomass separation in the Sirolan CF-B activated sludge system.

Optimisation of the Sirolan CF-B reactor system for nitrification – denitrification by utilisation of the provided anoxic selector zone.

Quantification of pesticide degradation in the full-scale biological treatment system operating at Kaputone Wool Scour, Christchurch:

- Quantification of pesticide removal by Sirolan CF vs CF-B.
- Confirm link of pesticide removal to wool grease removal.

Identification of the causes of foaming at low substrate concentration.

11 CONCLUSION

In this investigation up to 98% of the biodegradable fraction (measured as BOD_5) of primary wool scouring effluent pre-treated by chemical flocculation was shown to be removable by aerobic biological treatment in an activated sludge style system with 50 hours hydraulic residence time.

At high feed concentrations (e.g. > 3,000mg/L BOD_5) the chemically flocculated effluent was found to inhibit the effectiveness of the suspended biological culture in the completely mixed aerobic reactor. This inhibition was shown to approximately follow the two-part substrate inhibition model of Wayman and Tseng (Wayman *et al.* 1976) given as Equation (29) in Section 6.1.1, with a critical substrate concentration of 400mg/L BOD_5 in the mixed reactor liquor, above which substrate inhibition began to take effect. This effect was observed to occur both with feed neutralised to pH 7.0 and with feed at the normal operational pH of 3.3 – 4.5.

The standard substrate inhibition model proposed by Wayman and Tseng was modified by inclusion of pH inhibition kinetics based upon the pseudo-toxic concentration concept of Ko (Ko *et al.* 2001). This adjusted the maximum growth-rate term of the standard inhibition kinetic model as a function of deviation of operating pH from the nominal operating range of pH 6.5 – 8.0. This model accounted well for the detrimental effect of low pH on the effectiveness of the biological culture

Although the final kinetic model was verified as representative of the system tested, it is felt that this model should be treated cautiously when used in design calculations for development of a full-scale system. Kinetic analysis is primarily of use when designing the smallest possible system to achieve the task at hand. In the case of the treatment of wool scouring effluent, it is the belief of the author that the prime concern of the design process should be the stability and robustness of the process. Commercial units should therefore not be designed merely to meet the effluent quality parameters dictated by local regulatory authorities, but to do so under the most severe of transitory conditions that the treatment plant is expected to encounter.

Upon discovery that high feed concentration was toxic to the biological system, a significant amount of time was spent optimising the Sirolan CF chemical flocculation process to ensure

that the feed effluent to the bioreactor was of minimum possible BOD_5 content at all times. The key alterations made to the chemical flocculation process were to include an anaerobic bio-flocculation stage prior to chemical flocculation, and to apply a turbidity monitoring and control system to the product of the chemical flocculation plant. The inclusion of an anaerobic bio-flocculation stage, which essentially consisted of a 12 hour hydraulic residence time storage tank with bottom draw-off, gave a consistently higher quality product from the existing chemical flocculation system, with reduced chemical consumption in the chemical flocculation process. The turbidity monitoring and control system used the optical clarity of the product from the chemical flocculation process along with a purpose written PLC operating point search algorithm to ensure that the chemical flocculation plant was operating at maximum effectiveness at all times. Also included in the turbidity monitoring system was a high turbidity alarm, which diverted the bioreactor feed to the beginning of the pre-treatment process if its quality dropped below a certain minimum standard for biological processing.

One very economically beneficial property of this process, that was consistently observed from laboratory scale to 50,000L demonstration plant scale, was the ability of the biological culture growing in the aerobic reactor tanks to buffer the low pH feed effluent from the chemical flocculation process up to an operating pH of 8.0 – 8.5. At hydraulic residence times of 50 hours or more in the aerobic reactor, addition of caustic soda or other neutralising agents was only required when a significant increase in the feed rate or concentration (measured as BOD_5 or COD) was encountered. Under stable operating conditions with feed strength lower than 6,500mg/L BOD_5, the reactors trialled did not generally require supplemental neutralisation in order to maintain an operating pH of greater than 7.0. This self-neutralisation property of the biological process alone has the potential to save wool scours using the Sirolan CF process approximately $245,000 per year in effluent neutralisation chemicals (based on a 3m scour, operating 6,000hrs per year).

At pilot and demonstration plant scale, significant problems were encountered with foaming in the aerobic reactors. This problem was identified as worst at times of reduced or no feed to the process and, if left untreated, severely reduced the usable aeration capacity of the system.

Of the wide range of methods trialled for foam control, silicone based chemical antifoams and mechanical destruction of the foam by a centrifugal fan were found to be the most effective. The most effective antifoam used was Dow Corning RD Antifoam emulsion (10% active).

Mechanical foam destruction was best achieved by ducting the foam into a separate cyclonic chamber where gravity head, centrifugal force and shear force combined to break down the foam. Any foam that overflowed from this chamber had to pass through the centrifugal fan used to draw the foam from the reactor headspace, and was subsequently broken down to a liquid by contact with the fan's rotating blades.

While most of the kinetic and rate data for this investigation was collected under tightly controlled laboratory conditions with controlled feed quality, process verification and optimisation was carried out at both pilot plant scale and on a demonstration plant of sufficient size to handle the entire heavy effluent loading from a small wool scour. As both the pilot and demonstration plants were installed at an operational wool scour, feed rate and quality depended on upstream processing conditions in the scour and pre-treatment plant. This resulted in large day-to-day fluctuations in the quality of the feed to the bioreactors, which was shown to have a negative impact on the effectiveness of the biological process. In particular, under conditions of rapidly increasing feed effluent strength, the biological process was observed to struggle to maintain sufficient metabolic neutralisation of the feed acidity leading to catastrophic reactor failure if supplemental neutralisation chemicals (such as caustic soda) were not added to maintain pH > 6.5.

If buffer storage volume is to be added to the system to even out these feed fluctuations, it is recommended that the majority of the buffer volume be added prior to the Sirolan CF process. By having a large anaerobic storage tank prior to Sirolan CF, the bio-flocculation of feed to the effluent treatment plant is optimised, thus improving the consistency and quality of feed to the biological reactor. In some cases it may be particularly beneficial to maintain a small buffer tank between the chemical flocculation process and the biological reactor, as this would enable constant feed to the biological reactor to be maintained when the pre-treatment process is shut down. This latter option is particularly recommended if the pre-treatment process is not to be operated on a 24 hour / day basis.

Based on the results of this investigation a full-scale effluent treatment plant was designed by ADM Group Ltd Timaru. For process robustness and redundancy, two parallel aerobic reactor vessels were used. These were constructed as rectangular in-ground basins with a shared central wall. Each basin contained two venturi ejector aeration devices fed by a common submersible recirculation pump. Air was supplied to the two basins from a common centrifugal blower housed near the reactors.

Based on reduced effluent BOD_5, solids, and grease loadings, the described process is capable of saving the average wool scour in excess of NZ$1million per year in effluent discharge fees at a capital cost of NZ$1.3million ~ NZ$1.7million depending on plant capacity and site specific civil engineering requirements.

At the time of publishing three full-scale effluent treatment plants based on this research had been sold to ADM Group's clients in the scouring industry. Two of these clients were local, while the third was part of an export order worth in excess of NZ$5million which could not have gone ahead without the inclusion of this technology.

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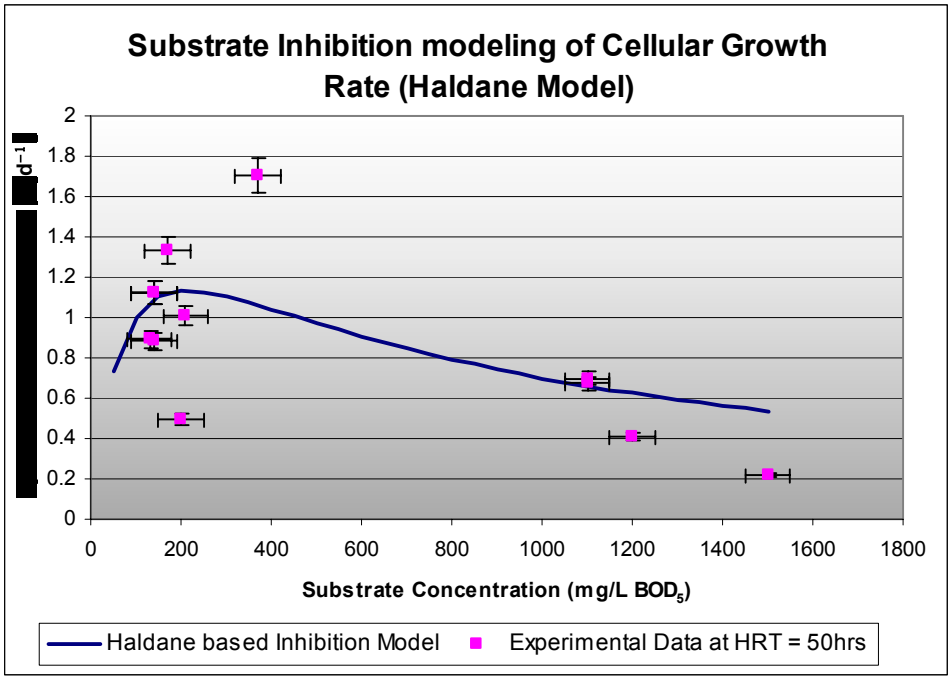
APPENDIX I

The following are the results of fitting the substrate inhibition models proposed in Section 6.1.1 to the experimental reaction rate data gathered using the 5L Bioflo3000 reactor.

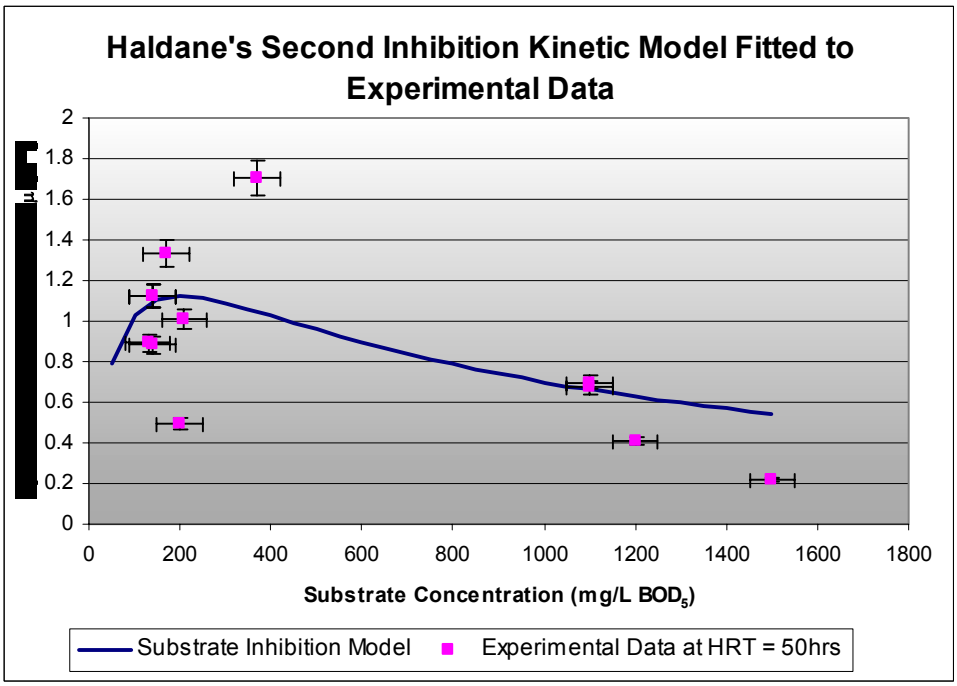
Haldane Model for Substrate Inhibition

$$\mu_{IS} = \frac{\hat{\mu} S}{(K_s + S + \frac{S^2}{K_{IS}})} \qquad (22)$$



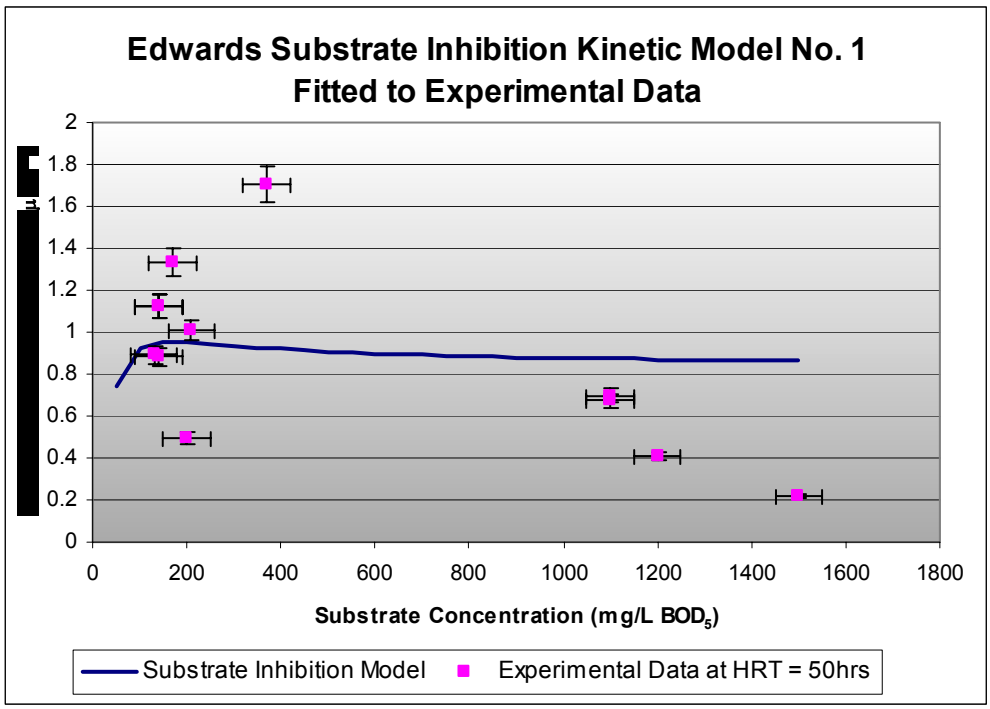
Haldane's second model for substrate inhibition

$$\mu_{IS} = \frac{\hat{\mu} S}{(K_s + S)(1 + \frac{S}{K_{IS}})} \qquad (24)$$

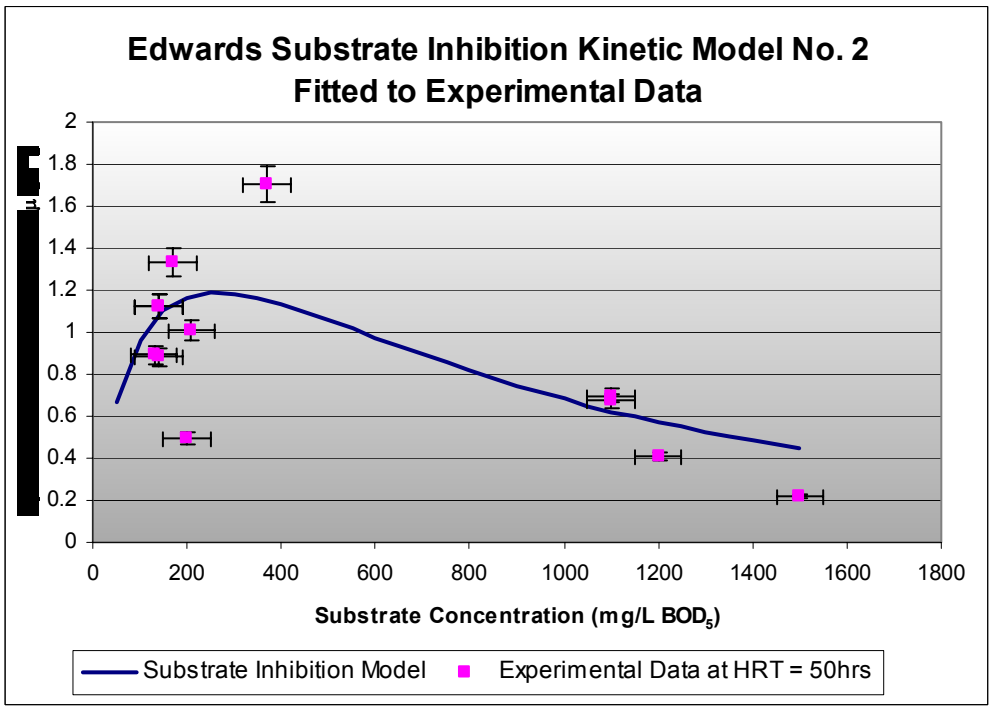


Equations (25) and (26) adapted from enzyme kinetics by Edwards (Edwards 1970) are fitted to experimental data below:

$$\mu_{IS} = \frac{\hat{\mu}\, S(1+\frac{S}{K_S})}{(K_s + S + \frac{S^2}{K_{IS}})} \qquad (25)$$

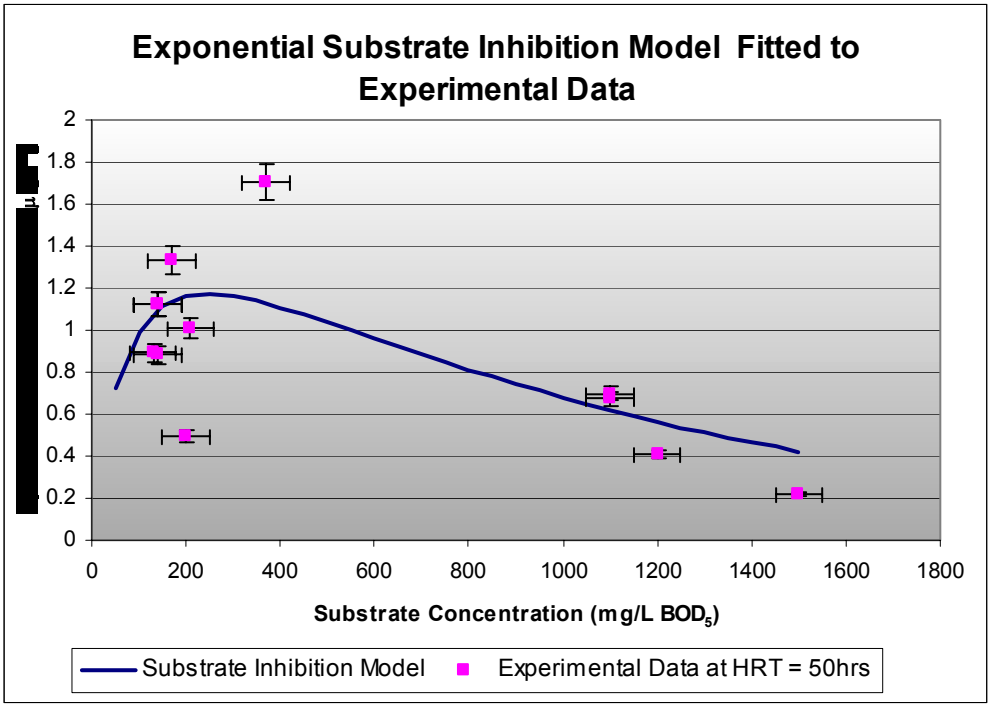


$$\mu_{IS} = \frac{\hat{\mu} S}{K_s + S + (\frac{S^2}{K_{IS}})(1+\frac{S}{K})} \qquad (26)$$

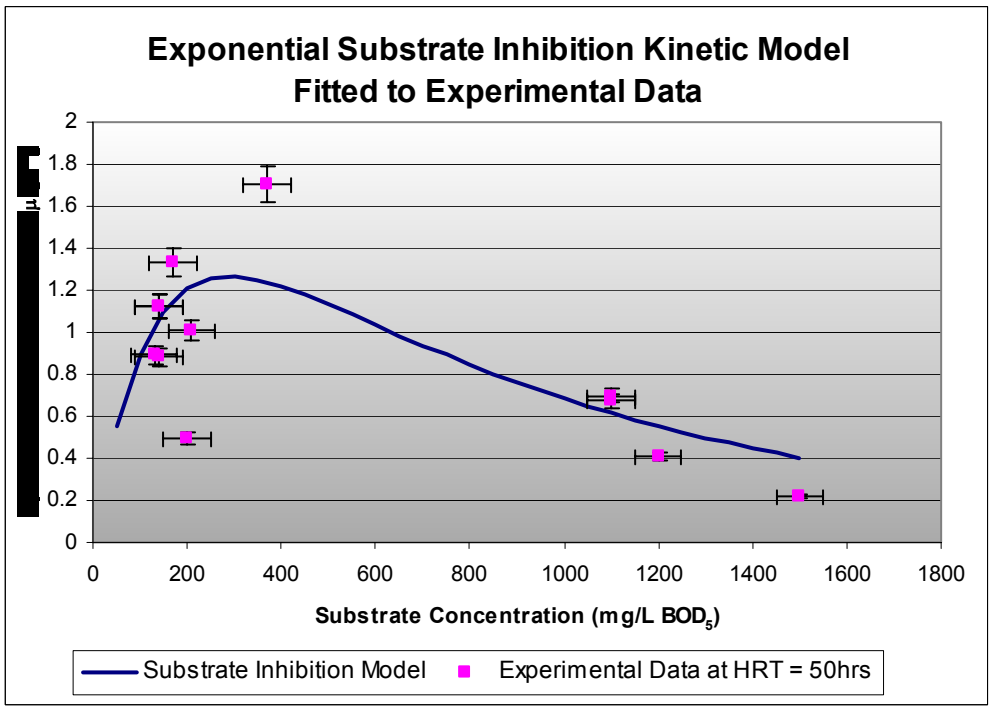


Exponential kinetic models fitted to experimental data

$$\mu_{IS} = \frac{\hat{\mu} S}{K_s + S} e^{-S/K_{IS}} \qquad (27)$$

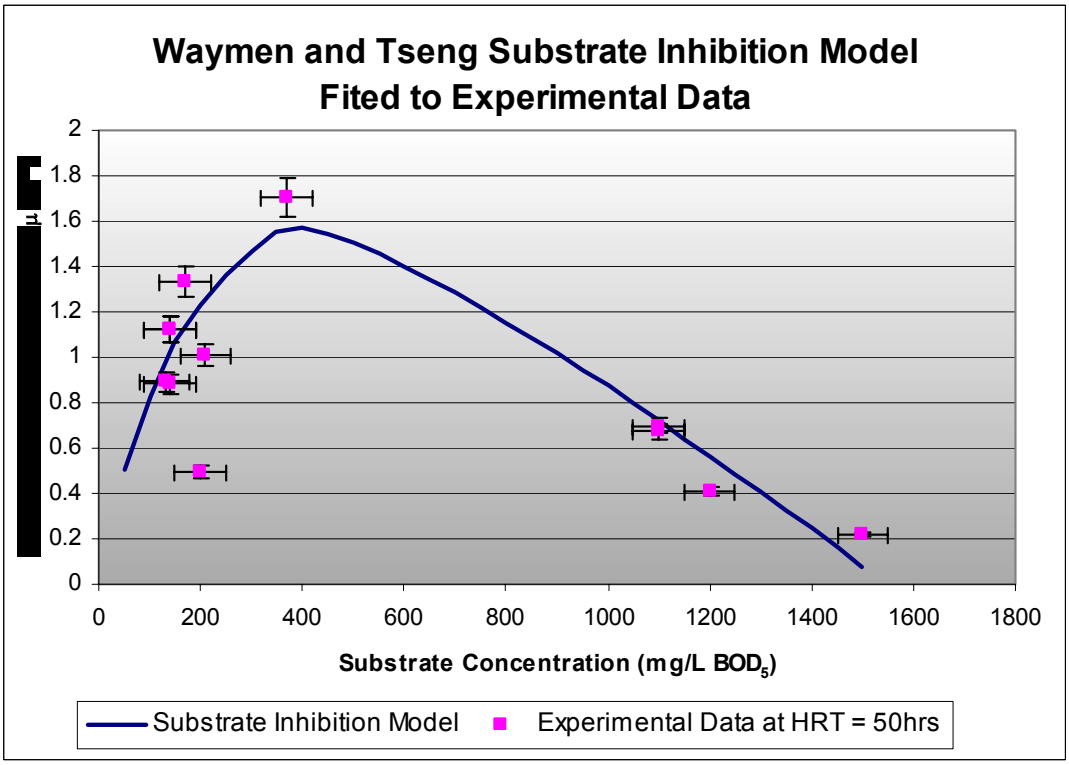


$$\mu_{IS} = \hat{\mu}(e^{-S/K_{IS}} - e^{-S/K_S}) \qquad (28)$$



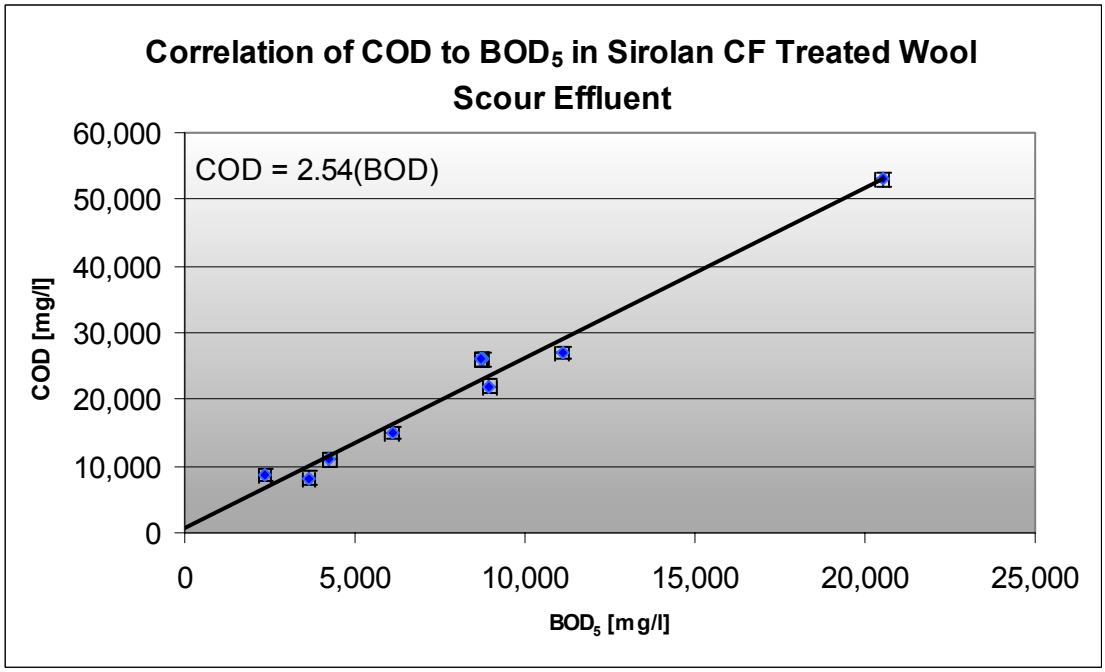
The Substrate inhibition model developed by Wayman and Tseng (Wayman *et al.* 1976) is given below (29), this predicted the experimental data obtained better than any of the other models given.

$$\left.\begin{aligned} \mu_{IS} &= \frac{\hat{\mu} S}{K_s + S} \quad when \quad S < S^* \\ \mu_{IS} &= \frac{\hat{\mu} S}{K_s + S} - K_{IS}(S - S^*) \quad when \quad S > S^* \end{aligned}\right\} \qquad (29)$$

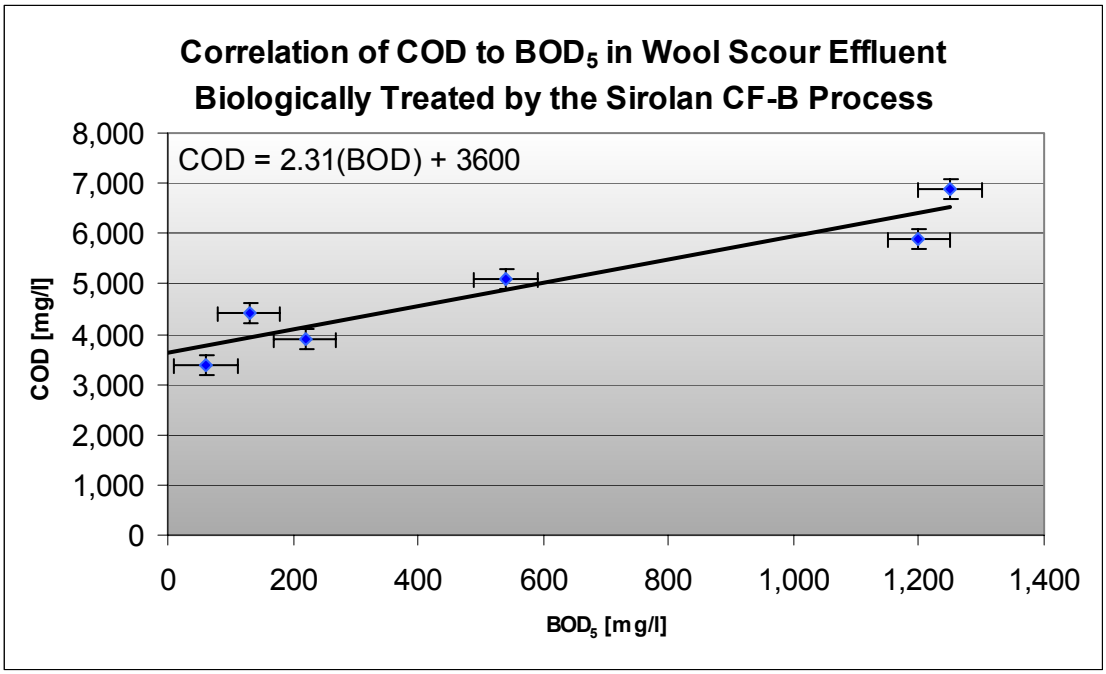


APPENDIX II

Throughout this thesis, both COD and BOD_5 are used to represent the quantity of oxidisable organic matter present in the effluent. For any given effluent type there is often a consistent correlation between these two parameters. In the case of raw and chemically treated wool scouring effluent, this relationship is relatively linear with COD generally being 2.3 ~ 3.2 times the BOD_5.



Once the effluent has been treated biologically, the ratio of COD / BOD_5 changes. This is because BOD_5 measures the biodegradable fraction of the oxidisable matter present in the effluent, while COD represents both the biodegradable, and non-biodegradable oxidisable matter in solution. By definition, a biological treatment process removes the biodegradable, and not the non-biodegradable fraction of the total oxidisable material in the effluent, therefore altering the ratio of COD / BOD_5. In the case of wool scouring effluent treated by the Sirolan CF and CF-B processes, even if all of the BOD_5 is removed, there still remains a significant fraction of COD in the effluent. This is the non-biodegradable fraction of the overall COD, and for wool scouring effluent this typically amounts to between 2,700 – 3,700mg/L COD. This is represented by the y-intercept in the plot on the next page.


Correlation of COD to BOD5 in Wool Scour Effluent
Biologically Treated by the Sirolan CF-B Process
COD = 2.31(BOD) + 3600
COD [mg/l]
8,000
7,000
6,000
5,000
4,000
3,000
2,000
1,000
0
0
200
400
600
800
1,000
1,200
1,400
BOD5 [mg/l]